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(54) HEAT-RESISTANT RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a heat-resistant resin composition having excellent thermal aging resistance and especially suitable as a liquid crystal substrate material, a semiconductor coating material and an adhesive for lens by compounding a cyclic olefin (co)polymer with a combination of specific antioxidants.

SOLUTION: The heat-resistant resin composition contains (A) a specific cyclic olefin (co)polymer and (B) at least one kind of antioxidant selected from (b-1) a phenolic antioxidant, (b-2) a phosphorus-based antioxidant and (b-3) a thioether-based antioxidant.

JP,2002-179875 Machine Translation

[Claim(s)]

[Claim 1](A) A cyclic olefin system (**) polymer including a repeating unit (a-1) shown with a following general formula (1), (B) Temperature of the 5% weight loss measured by thermogravimetric analysis (TGA) is an antioxidant which is not less than 250 **, (b-1) A heat resistant resin composition containing a phenolic antioxidant, the Lynn (b-2) system antioxidant, and (b-3) at least one sort of antioxidants chosen from a group of a sulfur-systems antioxidant.

[Formula 1]

[A¹ - A⁴ show independently a hydrogen atom, the alkyl group of the carbon numbers 1-20, a cycloalkyl group, an aryl group, an alkenyl group, a halogen atom, a halogenated hydrocarbon group, or the polar group expressed with -(CH₂)_kX among a general formula (1), respectively. Here, X is -C(O)OR¹ and -OC(O)R², R¹ - R² show a hydrogen atom, the alkyl group of the carbon numbers 1-20, an alkenyl group, an aryl group, cycloalkyl groups, and these halogenation groups, and k shows the integer of 0-3. The BINIRIDENIRU group formed in A¹ - A⁴ by A¹, A² or A³, and A⁴, The imido group formed by A¹, A² and A¹, A³ or A³, A⁴, and A² and A⁴ is also contained. l is an integer of 0 or 1.]

[Claim 2]The heat resistant resin composition according to claim 1 in which above-mentioned (A) cyclic olefin system (**) polymer includes a repeating unit (a-2) further shown with a following general formula (2).

[Formula 2]

[B¹ - B⁴ among a general formula (2), respectively independently, A hydrogen atom, the hydrocarbon group of the carbon numbers 1-20, and -(CR⁴R⁵)_nSi(OR³)_mR⁶_(3-m), (CR⁴R⁵) - Si(R⁷R⁸)OSi(OR³)_mR⁶_(3-m), -The alkoxy silyl groups expressed with C(O)O(CH₂)_nSi(OR³)_mR⁶_(3-m), allyloxy silyl groups, or such hydrolysis condensation residue are shown, At least one of B¹ - the B⁴ contains alkoxy silyl groups, allyloxy silyl groups, or such hydrolysis condensation residue. Here, R³ shows the alkyl group or aryl group of 1-10, and R⁴ - R⁸ show the hydrocarbon group of a hydrogen atom, a halogen atom, or the carbon numbers 1-20 independently, respectively. As for the integer of 0-3, and n, the integer of 0-5 and r of m are 0 or 1.]

[Claim 3]Above-mentioned claim 1 or the (A) cyclic olefin system (**) polymer according to claim 2, (B) Temperature of the 5% weight loss measured by thermogravimetric analysis (TGA) is an antioxidant which is not less than 250 **, (b-1) A heat resistant resin composition

containing at least one sort of antioxidants chosen from a group of the Lynn system antioxidant which consists of a hindered phenolic antioxidant, phosphite (b-2), and/or phosphate, and (b-3) a thioether series antioxidant.

[Claim 4] It is a repeating unit (a-2) above-mentioned (A) cyclic olefin system (**) polymer is indicated to be by the 50 - 99.9-mol % and above general formula (2) in a repeating unit (a-1) shown by the above-mentioned general formula (1) 50 - 0.1-mol % [(a-1) +(a-2) = 100-mol %] Included claim 1 - a heat resistant resin composition given in 3 any 1 paragraphs.

[Claim 5] Claim 1 - a heat resistant resin composition given in 4 any 1 paragraphs whose temperature of the 5% weight loss of the above-mentioned (B) antioxidant is not less than 300 **.

Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resin composition excellent in the heat resistance blended with the specific cyclic olefin system (**) polymer combining the specific antioxidant.

[0002]

[Description of the Prior Art] Conventionally, as transparent resin, polymethylmethacrylate, polycarbonate, polystyrene, 3-methylpentene resin, etc. are known. These resin is manufactured industrially and in large quantities, and is used in large quantities in each field taking advantage of the good transparency. However, these resin does not necessarily have enough heat resistance, and the glass transition temperature whose polycarbonate most used as heat-resistant high resin, for example among the above-mentioned resin is also the heat-resistant index is about 150 **. Development of resin with higher heat resistance is desired.

[0003] It excels in transparency and the ring-opening-polymerization object of the norbornene derivative which has a polar substituent is proposed as resin with higher heat resistance. However, the ring-opening-polymerization object of the norbornene derivative was not put in practical use as heat-resistant polymer, although the oxidation degradation under an elevated temperature was intense and had a high glass transition temperature, since it had a carbon-carbon double bond in the main chain. For this reason, the trial which improves that oxidation degradation nature is proposed by carrying out hydrogenation of the above-mentioned ring-opening-polymerization object (JP,57-8815,B). Although the improvement of the oxidation degradation nature by this hydrogenation can raise that anti-oxidation degradation nature substantially compared with the conventional non-hydropolymerization object, in the case of high-heat-resistance resin with a high glass transition temperature, it is necessary to make working temperature high inevitably -- this sake -- degradation at the time of processing, especially yellowing -- coloring still poses a problem.

[0004] The cyclic olefin system (**) polymer produced by carrying out addition condensation of the norbornene derivative is proposed in recent years (JP,4-63807,A, JP,8-198919,A, the Patent Publication Heisei No. 508649 [nine to] gazette, the Patent Publication Heisei No. 505880 [11 to] gazette, etc.). This cyclic olefin system (**) polymer is excellent in heat resistance and transparency, and useful in an optical material, a semiconductor coating material, adhesives, etc. however -- it is high-heat-resistance resin which has a high glass transition temperature, and it is necessary to make working temperature high inevitably like the ring-opening-polymerization object of the above-mentioned norbornene derivative, -- this sake -- degradation at the time of

processing, especially yellowing -- coloring still poses a problem.

[0005]

[Problem(s) to be Solved by the Invention] This invention by having been made against the background of the technical problem of the above-mentioned conventional technology, and blending with a cyclic olefin system (**) polymer combining a specific antioxidant, It excels in heat-resistant degradation nature, and aims at providing liquid crystal substrate material, semiconductor coating material, and the suitable heat resistant resin composition for the adhesives of a lens especially.

[0006]

[Means for Solving the Problem] A cyclic olefin system (**) polymer in which this invention includes a repeating unit (a-1) shown with the (A) following general formula (1), (B) Temperature of the 5% weight loss measured by thermogravimetric analysis (TGA) is an antioxidant which is not less than 250 **, (b-1) It is related with a heat resistant resin composition containing a phenolic antioxidant, the Lynn (b-2) system antioxidant, and (b-3) at least one sort of antioxidants chosen from a group of a sulfur-systems antioxidant.

[0007]

[Formula 3]

[0008] [A¹ - A⁴ show independently a hydrogen atom, the alkyl group of the carbon numbers 1-20, a cycloalkyl group, an aryl group, an alkenyl group, a halogen atom, a halogenated hydrocarbon group, or the polar group expressed with -(CH₂)_kX among a general formula (1), respectively. Here, X is -C(O) OR¹ and -OC(O) R², R¹ - R² show a hydrogen atom, the alkyl group of the carbon numbers 1-20, an alkenyl group, an aryl group, cycloalkyl groups, and these halogenation groups, and k shows the integer of 0-3. The BINIRIDENIRU group formed in A¹ - A⁴ by A¹, A² or A³, and A⁴, The imido group formed by A¹, A² and A¹, A³ or A³, A⁴, and A² and A⁴ is also contained. l is an integer of 0 or 1.]

Above A thing including a repeating unit (a-2) further shown in (A) cyclic olefin system (**) polymer with a following general formula (2) is preferred.

[0009]

[Formula 4]

[0010] [B¹ - B⁴ among a general formula (2), respectively independently, A hydrogen atom, the hydrocarbon group of the carbon numbers 1-20, and -(CR⁴R⁵)_nSi(OR³)_mR⁶_(3-m), (CR⁴R⁵) - Si(R⁷R⁸) OSi(OR³)_mR⁶_(3-m), -The alkoxy silyl groups expressed with C(O) O(CH₂)_nSi(OR³)_mR⁶

(3-m), allyloxy silyl groups, or such hydrolysis condensation residue are shown, At least one of B¹ - the B⁴ contains alkoxy silyl groups, allyloxy silyl groups, or such hydrolysis condensation residue. Here, R³ shows the alkyl group or aryl group of 1-10, and R⁴ - R⁸ show the hydrocarbon group of a hydrogen atom, a halogen atom, or the carbon numbers 1-20 independently, respectively. As for the integer of 0-3, and n, the integer of 0-5 and r of m are 0 or 1.]

Above-mentioned (A) cyclic olefin system (**) polymers are a repeating unit (a-2) shown by the 50 - 99.9-mol % and above general formula (2) in a repeating unit (a-1) shown by the above-mentioned general formula (1) 50 - 0.1-mol % [(a-1) +(a-2) = 100-mol %] Containing is preferred.

[0011]

[Embodiment of the Invention](A) (A) cyclic olefin system (**) polymer used for cyclic olefin system (**) polymer this invention is a polymer (**) of a cyclic olefin system including the repeating unit (a-1) shown in the above-mentioned general formula (1), and the repeating unit (a-2) further shown in the required ***** above-mentioned general formula (2).

[0012]Here, although 2 and 3 addition structural unit the above-mentioned repeating unit (a-1) is indicated to be to the above-mentioned general formula (1) are mentioned, a little 2 and 7 addition structural units which are shown in a following general formula (3) may be included in the repeating unit (a-1).

[0013]

[Formula 5]

[0014][A¹ - A⁴, and l are the same as that of what is shown in the above-mentioned general formula (1) respectively among a general formula (3).]

[0015]Hereafter, (A) cyclic olefin system (**) polymer used for this invention is explained still more concretely. A repeating unit (a-1) used for (A) cyclic olefin system (**) polymer of this invention can be formed by addition condensation of cyclic olefin (henceforth "specific cyclic olefin (1)") shown in a following general formula (4).

[0016]

[Formula 6]

[0017][A¹ - A⁴, and l are the same as that of what is shown in the above-mentioned general formula (1), respectively among a general formula (4).]

[0018]As an example of such specific cyclic olefin (1), 2-norbornene, 5-methyl-2-norbornene, 5-ethyl-2-norbornene, 5-propyl-2-norbornene, 5-butyl-2-norbornene, 5-pentyl-2-norbornene, 5-hexyl-2-norbornene, 5-heptyl-2-norbornene, 5-octyl-2-norbornene, 5-decyl-2-norbornene, 5-

dodecyl-2-norbornene, 5,6-dimethyl- 2-norbornene, 5-methyl, 5-ethyl-2-norbornene, 5-phenyl-2-norbornene, 5-vinyl-2-norbornene, 5-allyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-ethylidene-2-norbornene, 5-cyclohexyl-2-norbornene, 5-fluoro-2-norbornene, 5-chloro-2-norbornene, and 5-norbornene 2-methyl carboxylic acid, 5-norbornene 2-carboxylic acid ethyl, 5-norbornene 2-carboxylic acid butyl, 2-methyl, 5-norbornene 2-methyl carboxylic acid, 2-methyl, 5-norbornene 2-carboxylic acid ethyl, 2-methyl, 5-norbornene 2-carboxylic acid propyl, 2-methyl, 5-norbornene 2-carboxylic acid butyl, 2-methyl, 5-norbornene 2-carboxylic acid trifluoroethyl, 2-methyl, 5-norbornene 2-yl ethyl acetate, 5 - Spiro [norbornene 2-spiro N-phenylsuccinimide 5-norbornene 2-/ N] - Cyclohexylsuccinimide 5-norbornene 2-spiro N-methylsuccinimide 5-norbornene 2, 3-N-phenyl dicarboxyimide 5-norbornene 2,3-N-cyclohexyl dicarboxyimide acrylic acid 2-methyl-5-norbornene, Methacrylic acid 2-methyl-5-norbornene and 5-norbornene 2,3-dimethyl dicarboxylate, 5-norbornene 2,3-diethyl dicarboxylate, 3-tricyclo [4.3.0.1^{2,5}] Decene, 3, 7-tricyclo [4.3.0.1^{2,5}] Decadiene (dicyclopentadiene) 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] Dodecen, 8-methyl, 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] Dodecen, 8-methyl, 8-carbomethoxy, 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] Dodecen, 8-methyl, 8-ethoxycarbonyl, 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] Dodecen etc. can be mentioned.

[0019]A compound shown in the above-mentioned general formula (4) which forms the above-mentioned repeating unit (a-1) can be independent one sort, or can be used combining two or more sorts.

[0020]a rate in all the repeating units of the above-mentioned repeating unit (a-1) -- desirable -- 50-99.9-mol % -- further -- desirable -- 80-99.5-mol % -- especially -- desirable -- 90-98-mol % - it contains. It is it easy to hydrolyze a polymer to be less than [50 mol %], and formation of a film and a sheet becomes difficult. On the other hand, formation of a bridging body becomes difficult at the same time a fall of adhesion to metal substrates, such as a fall of film strength, Si, aluminum, Au, and Cu, etc. will arise, if 99.9-mol % is exceeded.

[0021]a repeating unit (a-2) shown in the above-mentioned general formula (2) -- (**) -- it is formed by carrying out addition copolymerization of the cyclic olefin (henceforth "specific cyclic olefin (2)") shown in a following general formula (5) to specific cyclic olefin (1) of the above-mentioned general formula (4). As other methods, (**) 5-trichlorosilyl 2-norbornene, 5-dichloromethylsilyl 2-norbornene, 5-dichloroethylsilyl 2-norbornene, 5-norbornene 2-carboxylic acid trichlorosilyl propyl, 2-methyl, 5-norbornene 2-carboxylic acid trichlorosilyl propyl, After carrying out addition copolymerization of specific cyclic olefin (3) which has which trichlorosilyl group and a dichloro alkyl silyl group, and the specific cyclic olefin (1), (**) By making it react with an alkoxide of a trichlorosilyl group in an obtained copolymer or a dichloro alkyl silyl group, and an alkaline metal, or Ali Loki Cyd of an alkaline metal, It is formed by making it react to alcohol or phenols under existence of an amine compound as other methods (low 2).

[0022]

[Formula 7]

[0023][B¹ - B⁴, and r are the same as that of what is shown in the above-mentioned general

formula (2) among a general formula (5).]

[0024]As an example of such specific cyclic olefin (2), 5-trimethoxysilyl 2-norbornene, 5-dimethoxy, chlorosilyl 2-norbornene, 5-methoxy, chloro, methylsilyl 2-norbornene, 5-dimethoxy, chlorosilyl 2-norbornene, 5-methoxy, a hydride, methylsilyl 2-norbornene, 5-dimethoxy, hydride silyl 2-norbornene, 5-methoxy dimethylsilyl 2-norbornene, 5-triethoxy silyl 2-norbornene, 5-diethoxy, chlorosilyl 2-norbornene, 5-ethoxy, chloro, methylsilyl 2-norbornene, 5-diethoxy, hydride silyl 2-norbornene, 5-ethoxy dimethylsilyl 2-norbornene, 5-ethoxydiethylsilyl 2-norbornene, 5-propoxy dimethylsilyl 2-norbornene, 5-triphenoxy silyl 2-norbornene, 5-diphenoxymethylsilyl 2-norbornene, 5-trimethoxysilyl methyl-2-norbornene, 5-(2-trimethoxysilyl) ethyl-2-norbornene, 5-(2-dimethoxy, chlorosilyl) ethyl-2-norbornene, 5-(1-trimethoxysilyl) ethyl-2-norbornene, 5-(2-trimethoxysilyl) propyl-2-norbornene, 5-(1-trimethoxysilyl) propyl-2-norbornene, 5-triethoxy silyl ethyl-2-norbornene, 5-dimethoxymethylsilylmethyl-2-norbornene, 5-trimethoxy propylsilyl 2-norbornene, 5-norbornene 2-carboxylic acid trimethoxysilylpropyl, 5-norbornene 2-carboxylic acid triethoxy silyl propyl, 5-norbornene 2-carboxylic acid dimethoxy, methylsilylpropyl, 2-methyl, 5-norbornene 2-carboxylic acid trimethoxysilylpropyl, 2-methyl, 5-norbornene 2-carboxylic acid dimethoxy, methylpropyl, 2-methyl, 5-norbornene 2-carboxylic acid triethoxy silyl propyl, etc. are mentioned.

[0025]By a repeating unit (a-2) being included at a moderate rate in a cyclic olefin system (**) polymer of this invention, while adhesion and adhesion to metal are improved, material which was excellent in solvent resistance by hydrolysis and crosslinking reaction can be obtained. a rate in all the repeating units of the above-mentioned repeating unit (a-2) -- desirable -- 0.1-50-mol % -- further -- desirable -- 0.5-20-mol % -- it is 2-10-mol % especially preferably. Less than [0.1 mol %], the content becomes insufficient [the above-mentioned effect]. On the other hand, if 50-mol % is exceeded, by alkoxy silyl groups which exists superfluously in a cyclic olefin system (**) polymer, allyloxy silyl groups, or such hydrolysis condensation residue. (**) It is easy to hydrolyze a polymer, and preservation stability will become bad, and it will not become what has the smooth surface of a sheet film.

[0026]A polymerization method of specific cyclic olefin (1) of this invention or a copolymerization method of cyclic olefin (1) and cyclic olefin (2) is performed by a following method. As a polymerization catalyst, a catalyst which forms a cation complex or cation complexes, such as periodic table 8 fellows' nickel, Pd, and Co, is usually used. As a typical thing, $[Pd(CH_3CN)_4][BF_4]_2$, $[Pd(PhCN)_4][SbF_6]$ Di-mu-chloro-screw (bicyclo [6-methoxy]) [2.2.1]Hept 2-ene- and 5sigma, 2piPd (it abbreviates to "I" hereafter.), I, methylalumoxane (it abbreviates to MAO hereafter) and I, $AgSbF_6$ and I, and $AgBF_4$, $[(\eta^3\text{-aryl})PdCl]_2$ and $AgSbF_6$, $[(\eta^3\text{-aryl})PdCl]_2$ and $AgBF_4$, $[(\eta^3\text{-clo chill})Pd(\text{cyclo-octadiene})][PF_6]$ $^{**}[(1, 5\text{-cyclo-octadiene})Pd(Cl)(CH_3)]PPh_3$ and NaB [3, 5-(CF_3) $_2C_6H_3$] $_4$, $[(\eta^3\text{-clo chill})nickel(\text{cyclo-octadiene})][B(CF_3)(C_6H_4)_4]$ $^{**}[NiBr(NPMe_3)]_4$, MAO and nickel(octoate) $_2$, MAO and nickel(octoate) $_2$, $B(C_6F_5)_3$, and $AlEt_3$, nickel(octoate) $_2$, a reactant of $HSbF_6$, BF_3 and Et_2O , and $AlEt_3$, A reactant of nickel(octoate) $_2$, a reactant of $HSbF_6$, BF_3 and Et_2O , and $AlEt_3$, nickel(octoate) $_2$, a reactant of $HSbF_6$, and $AlEt_2F$, A reactant and $AlEtF_2$ of nickel(octoate) $_2$ and $HSbF_6$, nickel(naphthoate) $_2$, a reactant of $HSbF_6$, BF_3 and Et_2O , and $AlBu_3$, A reactant of nickel(naphthoate) $_2$, a reactant of $HSbF_6$, $B(C_6F_5)_3$, and $AlEt_3$, nickel(octoate) $_2$, $Ph_3C-B(C_6F_5)_3$, $AlEt_3$, Toluene-nickel(C_6F_5) $_2$, Xylene-nickel(C_6F_5) $_2$, Mesitylene-nickel(C_6F_5) $_2$, Co (neo decanoate), MAO, etc. are mentioned.

[0027]As a solvent, alicyclic hydrocarbon solvents, such as cyclohexane, cyclopentane, and

methylcyclopentane, Aliphatic hydrocarbon solvents, such as pentane, hexane, heptane, and octane, Aromatic hydrocarbon solvents, such as toluene, benzene, and xylene, dichloromethane, Halogenated hydrocarbon solvents, such as 1,2-dichloroethylene and chlorobenzene, Ethyl acetate, butyl acetate, gamma-butyrolactone, propylene glycol, A solvent chosen from polar solvents, such as wood ether, nitromethane, N-methyl pyrrolidone, pyridine, N,N'-dimethylimidazolidinone, dimethylformamide, and an acetamide, etc. is used.

[0028]As the method of a polymerization, under nitrogen or argon atmosphere, a monomer and a molecular weight modifier which become a reaction vessel from a solvent and cyclic olefin are taught, and a polymerization system is set as temperature of the range of -20 to 100 **. Next, the above-mentioned catalyst component is added and it polymerizes in -20 to 100 **. A weight ratio of a solvent/monomer is performed in 1-20. Regulation of a molecular weight is adjusted by the target molecular weight with an inversion rate and polymerization temperature to quantity of a polymerization catalyst, an addition of molecular weight modifiers, such as alpha olefin, hydrogen, and a diphenyl dihydrosilane, and a polymer (**). A stop of a polymerization is performed by water, alcohol, organic acid, carbon dioxide, etc. (**) The water/alcoholic mixture of acid chosen as a polymer solution from maleic acid, fumaric acid, and oxalic acid are added, and a catalyst residue is separated and removed from a polymer solution (**). (**) A polymer is obtained by putting a polymer solution (**) in alcohol chosen from methanol, ethanol, isopropanol, etc., solidifying it, and carrying out reduced pressure drying. At this process, an unreacted monomer which remains in a polymer solution (**) is also removed.

[0029]A molecular weight of (A) cyclic olefin system (**) polymer used for this invention, By polystyrene conversion measured by gel permeation chromatogram used as a solvent, o-dichlorobenzene. It is desirable and a number average molecular weight is [5,000-1,000,000, and weight average molecular weight] preferred to 10,000-1,500,000, and a pan, a number average molecular weight is 10,000 to 700,000, and weight average molecular weight is 20,000-1,000,000. Disruptive strength when a number average molecular weight uses less than 5,000 and weight average molecular weight considers it as a film, a thin film, and a sheet by less than 10,000 becomes insufficient in many cases. On the other hand, if a number average molecular weight exceeds 1,000,000 and weight average molecular weight exceeds 1,500,000, Since a problem of insoluble matter to a cast solvent in which the molding workability of a sheet obtained and a film falls, and solution viscosity becomes high at the time of cast film film production increasing arises, handling becomes difficult.

[0030]150 ** - 400 ** of glass transition temperature [250-380 ** of / 270-370 ** of] of (A) cyclic olefin system (**) polymer of this invention is 300-350 ** especially preferably still more preferably preferably. Here, glass transition temperature of (A) cyclic olefin system (**) polymer of this invention is called for with peak temperature of temperature distribution of T_{δ} measured by dynamic viscoelasticity. (Storage-modulus E' , loss-modulus E'' ($T_{\delta} = E''/E'$)) Less than 150 ** of heat resistance is [the glass transition temperature] insufficient, and if glass transition temperature exceeds 400 ** on the other hand, problems, like film body formation which breaks easily becomes difficult will arise.

[0031](B) An antioxidant, next the (B) antioxidant used for a heat-resistant constituent of this invention are at least one sort chosen from a group of a phenolic antioxidant (b-1), the Lynn (b-2) system antioxidant, and (b-3) a thioether series antioxidant.

[0032](b-1) Phenolic antioxidant; (b-1) it is the feature that an alkyl group which has a straight chain or branching ($C_1 - C_{20}$) has replaced a phenolic antioxidant by the 2nd place of a phenolic group and/or the 6th place. As an example of (b-1), it is pentaerythrityl tetrakis. [3-(3,5-di-t-

butyl-4-hydroxyphenyl) propionate] 3,9-screw {2 - [3-(3-t-butyl-4-hydroxy-5-methylphenyl) propionyloxy] -1,1-dimethylethyl} 2, 4 and 8, 10-tetraoxaspiro [5, 5] An undecane, octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, 1,6-hexane *****-**** [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] 1,3,5-trimethyl 2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) benzene, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-t-butyl-4-ethylphenol, 2,6-diphenyl-4-octadecyloxyphenol, stearyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate, distearyl (3,5-di-t-butyl-4-hydroxybenzyl) phosphonate, a thiodiethylene glycol screw [(3,5-di-t-butyl-4-hydroxyphenyl) Propionate] A 4,4'-thioscrew (6-t-butyl-m-cresol), 2-octylthio 4,6-JI (3,5-di-t-butyl-4-hydroxyphenoxy)-s-triazine, 2,2'-methylenebis (4-methyl-6-t-butyl-6-butylphenol), 2, - 2'-methylenebis (4-ethyl-6-t-butylphenol), a screw [3,3-bis(4-hydroxy-3-t-butylphenyl)butyric acid] Glycol ester, 4,4'-butylidenebis (6-t-butyl-m-cresol), A 2,2'-ethylidenescrew (4,6-di-t-butylphenol), a 2,2'-ethylidenescrew (4-s-butyl-6-t-butylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, a screw [2-t-butyl-4-methyl-6-(2-hydroxy-3-t-butyl-5-methylbenzyl) phenyl] Terephthalate, 1,3,5-tris (2,6-dimethyl- 3-hydroxy-4-t-butylbenzyl) isocyanurate, 1,3,5-tris (3,5-di-t-butyl-4-hydroxybenzyl)-2,4,6-trimethyl benzene, 1 and 3, 5-tris [(3,5-di-t-butyl-4-hydroxyphenyl) Propionyloxy ethyl] Isocyanurate, tetrakis [Methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] Methane, 2-t-butyl-4-methyl-6-(2-acryloyloxy 3-t-butyl-5-methylbenzyl) phenol, a 3,9-bis(1,1-dimethyl- 2-hydroxyethyl)-2,4,8,10-tetraoxaspiro [5, 5] undecane-screw [beta-(3-t-butyl-4-hydroxy-5-methylphenyl) propionate] Triethylene glycol screw [beta-(3-t-butyl-4-hydroxy-5-methylphenyl) propionate] 1,1'-bis(4-hydroxyphenyl)cyclohexane, 2,2'-methylenebis (4-methyl 6-t-butylphenol), 2,2' **MECHIREMBISU (4-ethyl 6-t-butylphenol), 2,2' **MECHIREMBISU (6-(1-methylcyclohexyl)-4-methyl phenol), 4,4' **BUCHIRIDEMBISU (3-methyl 6-t-butylphenol), 3,9-screw (2-(3-t-butyl 4-hydroxy 5-methylphenyl PUROPIONIROKISHI) 1,1 **JIME chill ethyl) - 2, 4 and 8, 10 **TETORA oxaspiro (5, 5) undecane, 4,4'-thiobis(3-methyl-6-t-butylphenol), 4,4' **BISU (3,5 **JI t-butyl 4-hydroxybenzyl) sulfide, 4,4' **CHIOBISU (6-t-butyl 2-methyl phenol), 2,5-di-t-butylhydroquinone, 2,5-G t-amyl hydroquinone and 2-t-butyl 6-(3-t-butyl 2-hydroxy 5-methylbenzyl)-4-methylphenyl acrylate and 2,4-dimethyl 6-(1-methylcyclohexyl and SUCHIRENEITIDDO phenol.) 2,4-bis(octylthio)(methyl)-5-methyl phenol etc. are mentioned. In these, a hindered phenolic antioxidant is preferred.

[0033](b-2) Lynn system antioxidant; (b-2) the Lynn system antioxidant is phosphate which is phosphorus compounds of III value, or phosphate. As an example, bis-(2,6-di-t-butyl-4-methylphenyl)penta pentaerythritoldiphosphite, Tris (2,4-di-t-butylphenyl phosphite), tetrakis (2,4-G t-butyl 5-methylphenyl) - 4 and 4' **BIFENI range phospho night, 3,5-di-t-butyl-4-hydroxybenzyl phosphonate diethyl ester, Bis-(2,6-JIKUMIRU phenyl)pentaerythritoldiphosphite, 2,2-methylene bis(4,6-di-t-butylphenyl)octyl phosphite, Tris (mixed mono- and di-nonylphenyl phosphite), Bis(2,4-di-tert-butylphenyl) penta pentaerythritol di-phosphite, Bis(2,6-di-t-butyl-4-carbomethoxyethyl-phenyl)pentaerythritoldiphosphite, bis(2,6-di-t-butyl-4-octadecyl oxycarbonyl ethyl-phenyl)pentaerythritoldiphosphite, etc. are mentioned. In these, phosphite and phosphate are preferred.

[0034]Thioether series antioxidant; (b-3) (b-3) As an example of a thioether series antioxidant, Dilauryl 3,3'-thiodipropionate, a bis(2-methyl 4-(3-n-dodecyl) thio propionyloxy)-5-t-butylphenyl sulfide, The distearyl 3, 3'-thiodipropionate, pentaerythritol tetrakis (3-lauryl) thiopropionate, etc. are mentioned.

[0035](B) Although an antioxidant is independent or the above-mentioned (b-1) phenolic antioxidant, the Lynn (b-2) system antioxidant, and a thioether series (b-3) antioxidant can be

used together and used for it, respectively, An ingredient (b-1), (b-2), or (b-3) two or more sorts of concomitant use systems of an ingredient are preferably preferred. Not less than 250 ** is required for temperature of a decrease of 5% weight in thermogravimetric analysis (TGA) of these antioxidants, and it is preferred. [of not less than 300 more **] That whose temperature of a decrease of 5% weight is less than 250 ** will volatilize, when polymer is used at a not less than 150 ** elevated temperature, and an effect of an antioxidant of it will be lost.

[0036]The (B) ingredient of a using rate of (A) cyclic olefin system (**) polymer and the (B) antioxidant in a heat resistant resin composition of this invention is usually 0.3 - 3 weight section preferably 0.05 to 5 weight section to (A) ingredient 100 weight section. (B) If a using rate of an ingredient cannot acquire oxidation degradation preventive effect sufficient in less than 0.05 weight section but adds exceeding five weight sections on the other hand, deterioration of quality of a mechanical strength of a constituent obtained, glass transition temperature, etc., an increase in a volatile constituent at the time of heating, etc. arise, and it is not desirable.

[0037](A) As a method of adding these (B) antioxidants to a cyclic olefin system (**) polymer, How to add at the time of specific cyclic olefin (1), composition of (2), or refining, A method of adding to a cyclic olefin system (**) polymer solution, a method of adding at the time of refining of a ** (**) polymer, etc. are mentioned, and except adding to the polymer (**) itself, it can also add to a solvent etc. beforehand and is not limited in particular to them.

[0038]A norbornene system polymer and an addition polymer which are the hydrides of a ring-opening-polymerization object conventionally publicly known to (A) cyclic olefin system (**) polymer of this invention [For example, JP,61-29260,A, JP,60-16870,A, JP,60-26024,A, JP,2-51511,A, JP,1-132625,A, A polymer of statements, such as JP,1-132626,A, JP,4-202404,A, JP,4-63807,A, JP,8-198919,A, the Patent Publication Heisei No. 508649 [nine to] gazette, the Patent Publication Heisei No. 505880 [11 to] gazette, and JP,61-292601,A,] (**) Heat resistance and an optical property (transparency, low birefringence) excellent in a constituent produced by blending, and adhesion and adhesion can be given.

[0039]In such a constituent, although a blending ratio of (A) cyclic olefin system (**) polymer of this invention and other polymers is suitably chosen according to a kind of a polymer (**) of this invention, and other polymers, both compatibility, and the purpose of using a constituent, In order to obtain a constituent which has the outstanding heat resistance, a rate of (A) cyclic olefin system (**) polymer of this invention is 20 to 80 % of the weight especially preferably ten to 90% of the weight still more preferably five to 95% of the weight preferably.

[0040]moreover -- a heat resistant resin composition of this invention -- in addition, a range which does not spoil heat resistance for stabilizer which is effective in preventing degradation of resin by light -- one sort -- or two or more sorts may be combined and it may use. As an ultraviolet ray absorbent, a benzophenone series, a salicylate series, a benzotriazol system, etc. are mentioned among what is used as stabilizer. Below, an example of stabilizer is listed.

[0041]As amine system stabilizer, phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, Dioctyl phenylamine, N,N'-diphenyl-p-phenylenediamine, N' and N'-di-beta-naphthyl p-phenylene diamine, N-cyclohexyl-N'-phenyl-p-phenylene diamine, a 2-(3,5-t-butyl-4-hydroxybenzyl)-2-n-butylmalonic acid screw (1,2,2,6,6-pentamethyl 4-piperidyl) and poly -- { [6-(1,1,3,3-tetramethylbutyl) imino-1,3,5-triazine 2,4-diyl] [(2, 2, 6, and 6-tetramethyl 4-piperidyl) Imino] Hexamethylene[(2, 2, 6, and 6-tetramethyl 4-piperidyl) Imino] }, a succinate dimethyl 1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine polycondensation thing, bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)sebacate, etc. are mentioned.

[0042]As benzophenone series stabilizer, 2-hydroxybenzophenone, 2-hydroxy-4-

methoxybenzophenone, 2,4-dihydroxybenzophenone, 2,2', 4-trihydroxy benzophenone, 2,2', and 4,4'-tetrahydroxybenzophenone etc. are mentioned.

[0043]As salicylate series stabilizer, phenyl salicylate and 2,4-di-t-buthylphenyl 3' and 5'-di-t-butyl-4'-hydroxy benzoate, Phenyl-3,5-di-t-butyl-4-hydroxy benzoate and 2-methyl-4-t-buthylphenyl 3' and 5'-di-t-butyl-4'-hydroxy benzoate etc. are mentioned. [0044]As benzotriazol system stabilizer, 2-(2'-hydroxy-5'-methylphenyl) benzotriazol, A 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-t-buthylphenyl) benzotriazol, 2-(2'-hydroxy-5'-t-octylphenyl) benzotriazol, 2-(2'-3' and 5'-di-t-amyl phenyl) benzotriazol, etc. are mentioned.

[0045]As hydrazine system stabilizer, they are maleic hydrazide and a N,N'-screw. [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionyl] Hydrazine, N-salicyloyl N'-aldehyde hydrazine; etc. are mentioned.

[0046]As epoxy system stabilizer, epoxidation linseed oil, epoxidized soybean oil, epoxy butyl stearate, epoxy octyl stearate, epoxy lauryl stearate, a low-molecular-weight epoxy resin, etc. are mentioned. each above stabilizer -- one sort -- or two or more sorts are mixed and it is used.

[0047]In a heat resistant resin composition of this invention, if needed further High-class dicarboxylic acid metal salt, Lubricant, such as high-class carboxylate, a plasticizer, a spray for preventing static electricity, inorganic matter and organic system colorant, a foaming agent, inorganic matter and an organic system bulking agent, fire retardant other than the above, a surface gloss improving agent, a flattening, etc. can be added. These various additive agents can be added in a manufacturing process of a resin composition.

[0048]A heat resistant resin composition of this invention is obtained by mixing in a solvent (A) cyclic olefin system (**) polymer and the above-mentioned (B) antioxidant, and an additive agent used further if needed at the time of casting. As a casting solvent, what both (A) and (B) dissolve is preferred.

[0049]Although a heat resistant resin composition of this invention can be used alone, Glass fiber, a metal fiber since compatibility with various polar materials is good, It can also be used as composite materials, such as carbon fiber or these powder, calcium carbonate, talc, gypsum, alumina, silica, mica, CHITSU-ized boron, zirconia, silicon carbide, and potassium titanate.

[0050]A cyclic olefin system copolymer of this invention and a heat resistant resin composition of an antioxidant are suitable for plastic alternate material etc. of a use as which high heat resistance is required, for example, liquid crystal substrate glass. That is, heat resistance required of a substrate material can be satisfied at processes, such as exposure by TFT (thin film transistor) formation of a up to [a liquid crystal display substrate], development, and etching. Since a heat resistant resin composition of this invention has outstanding optical transparency, heat resistance, adhesion and adhesion, and moisture absorption resistance, It is used for electronic parts, such as a light guide plate, a polarization film, a liquid crystal panel, a phase difference film, a transparent conductive film, an OHP film, an optical disc, an optical fiber, and a lens, a medical care container, a container, etc.

[0051]

[Example]Although an example is given and this invention is explained still more concretely hereafter, this invention is not limited to the following examples. Among an example, a part and especially % are weight references, unless it refuses. The weight average molecular weight and the number average molecular weight in an example, intrinsic viscosity, and hue are measured as follows.

It measured at 120 ** by using o-dichlorobenzene as a solvent using H type column by TOSOH

CORP. with weight average molecular weight and the product made by number average molecular weight Waters (WATERS), and C [150] type gel-permeation-chromatography device. The obtained molecular weight is a standard polystyrene reduced property.

Hue various antioxidants were added to the polymer solution at the time of the cast, and the film was created by the cast method using the homogeneous solution. The obtained sample was used as the methylene chloride solution 15%, respectively, and the degree of yellow (YI value) was measured by the transmitted light according to JIS K7103.

[0052] It taught as synthetic example 1 monomer by 5-n-hexyl-2-norbornene 93.75 millimol, 2-norbornene 500 millimol, and 5-triethoxy silyl 2-norbornene 31.25 millimol, and 500 g of toluene was taught to the reactor with a capacity of 1 l. under nitrogen as a solvent. Adjust the system of reaction at 10 **, and Triethylaluminum 0.5 millimol, Boron trifluoride and diethylether (BF_3 and Et_2O) 0.4 millimol, It added to ****, 0.2 millimols of nickel compounds to which octanoic acid nickel and antimony hexafluoride acid (HSbF_6) were made to react by the mole ratio 1:1 at -15 ** beforehand finally were added with the nickel atom, and the polymerization was started. The polymerization was performed at 30 ** for 2 hours, and the polymerization was suspended by ethanol. The inversion rate to the copolymer was 89%. Lactic acid 60 millimol was added to this copolymer solution, and it was made to react to a catalyst component. The copolymer solution was put into 5 l. of isopropanol, the copolymer was solidified, and the unreacted monomer, the above-mentioned reaction reagent, and the catalyst residue were removed from the copolymer. The solidified copolymer was dried and the copolymer A was obtained. The content of the structural unit containing the triethoxy silyl group in A was 4.9-mol % from 270 MHz and ^1H -NMR analysis (4 ppm ETOKI silyl group methylene absorption, solvent: D-ized toluene, TMS standard). The content of the structural unit originating in 5-n-hexyl-2-norbornene was 14.0-mol % from the analytical curve by the characteristic absorption of 721 cm^{-1} of infrared analysis. The number average molecular weight of polystyrene conversion of measurement of GPC to the copolymer A was 200,000, and weight average molecular weight was 440,000.

[0053] In the example 1 of synthetic example 2 composition, except using 5-n-hexyl-2-norbornene 125 millimol and 2-norbornene 500 millimol, it carried out like the synthetic example 1 and the copolymer B was obtained. The inversion rate to the copolymer was 92%. The content of the structural unit originating in 5-n-hexyl-2-norbornene was 19.0-mol % from the analytical curve by the characteristic absorption of 721 cm^{-1} of infrared analysis. The number average molecular weight of polystyrene conversion of the copolymer B was 117,000, and weight average molecular weight was 270,000.

[0054] It is 5-n-hexyl-2-norbornene 93.75 millimol, 2-norbornene 500 millimol, 8-methyl, and 8-carbomethoxy-3-tetracyclo as synthetic example 3 monomer. [4.4.0.1^{2,5}1^{7,10}] Except using dodecen 31.25 millimol, it carried out like the synthetic example 1 and the copolymer C was obtained. The inversion rate to the copolymer was 75%. 8-methyl in C, 8-carbomethoxy-3-tetracyclo [4.4.0.1^{2,5}1^{7,10}] The percentage of the structure originating in dodecen was 4.9-mol % from the analytical curve by the characteristic absorption of infrared analysis 1730 cm^{-1} . The content of the structure originating in 5-n-hexyl-2-norbornene was 14.5-mol % from the analytical curve by the characteristic absorption of 721- cm^{-1} of infrared analysis. 158, 000, and the weight average molecular weight of the number average molecular weight of polystyrene conversion of C were 300,000.

[0055] Except using 5-n-hexyl-2-norbornene 93.75 millimol, 2-norbornene 500 millimol, and 5-ethylidene 2-norbornene 31.25 millimol as synthetic example 4 monomer, it carried out like the

synthetic example 1 and the copolymer D was obtained. The inversion rate to the copolymer D was 80%. The percentage of the structure unit originating in the 5-ethylidene 2-norbornene in D was 4.9-mol % by the iodination titrimetric method. The content of the structure originating in 5-n-hexyl-2-norbornene was 14.0-mol % from the analytical curve by the characteristic absorption of 721-cm^{-1} of infrared analysis. The number average molecular weight of the copolymer D was 138,000, and weight average molecular weight was 290,000.

[0056]The cyclic olefin system copolymer obtained in example of film production above-mentioned each synthetic example by the cast method was dissolved in toluene, and it prepared so that it might become TSC = 10%. kind antioxidant after filtrating this solution with the filter of a 1-micrometer mesh (b-1) (b-2) -- and -- (b-3) the following table 1 shows -- quantity addition was carried out and it was considered as the homogeneous solution. After applying this on a stainless steel board, the solvent was made to evaporate under a room temperature. The solvent which remains in a film by heat-treating the obtained film at 210°C under a vacuum for 2 hours was made to evaporate thoroughly, and the target bright film was obtained.

[0057]Example The bright film obtained by 1-23, the comparative example 1 - the 3 above-mentioned cast method was heated in the air, and change of hue (YI value) estimated anti-oxidation degradation nature. Tables 2-5 (b-2) (b-3) The details of various antioxidants used in inside (b-1) are as follows.

(b-1) ingredient; Phenolic antioxidant a: . Pentaerythrityl tetrakis [3-. 3. The 5-di-t-butyl-4-hydroxyphenyl propionate b:1, 3, 5-trimethyl 2 and 4, 6-tris. (3,5-di-t-butyl-4-hydroxybenzyl) benzene c:octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate d:2,6-di-tert-butyl-4-methylphenol (b-2) ingredient; -- Lynn system antioxidant e: . A screw. 2. the 6-di- t - butyl-4-methylphenyl pentaerythritol di-phosphite f:tetrakis (2,4-di-t-butyl-5-methylphenyl)-4,4'-biphenylene diphosphonate g: -- tris (2,4-di-t-buthylphenyl) Phosphite h: . 2,2-methylene-bis(4,6-di-t-butylphenyl)octyl-phosphite (b-3) ingredient; thioether series antioxidant i:bis(2-methyl-4-(3-n-dodecyl) thio propionyloxy)-5-t-buthylphenyl sulfide [0058]

[Table 1]

[0059]

[Table 2]

[0060]
[Table 3]

[0061]
[Table 4]

[0062]
[Table 5]

[0063]

[Effect of the Invention]By combining a specific antioxidant with the cyclic olefin system (**) polymer which has a glass transition temperature high enough, the coloring which takes place by oxidation degradation is improved substantially, and the heat resistant resin composition of this invention solves the problem of the yellow discoloration under the severe condition which poses a problem conventionally. by development of this art, the semiconductor encapsulant etc. which have impossible plastic-izing of the glass substrate of TFT liquid crystal, and high heat resistance and transparency in respect of heat resistance become possible by old resin.

TECHNICAL FIELD

[Field of the Invention]This invention relates to the resin composition excellent in the heat resistance blended with the specific cyclic olefin system (**) polymer combining the specific antioxidant.

[Description of the Prior Art]Conventionally, as transparent resin, polymethylmethacrylate, polycarbonate, polystyrene, 3-methylpentene resin, etc. are known. These resin is manufactured industrially and in large quantities, and is used in large quantities in each field taking advantage of the good transparency. However, these resin does not necessarily have enough heat resistance, and the glass transition temperature whose polycarbonate most used as heat-resistant high resin, for example among the above-mentioned resin is also the heat-resistant index is about 150 **. Development of resin with higher heat resistance is desired.

[0003]It excels in transparency and the ring-opening-polymerization object of the norbornene derivative which has a polar substituent is proposed as resin with higher heat resistance. However, the ring-opening-polymerization object of the norbornene derivative was not put in practical use as heat-resistant polymer, although the oxidation degradation under an elevated temperature was intense and had a high glass transition temperature, since it had a carbon-carbon double bond in the main chain. For this reason, the trial which improves that oxidation degradation nature is proposed by carrying out hydrogenation of the above-mentioned ring-opening-polymerization object (JP,57-8815,B). Although the improvement of the oxidation degradation nature by this hydrogenation can raise that anti-oxidation degradation nature substantially compared with the conventional non-hydropolymerization object, in the case of high-heat-resistance resin with a high glass transition temperature, it is necessary to make working temperature high inevitably -- this sake -- degradation at the time of processing, especially yellowing -- coloring still poses a problem.

[0004]The cyclic olefin system (**) polymer produced by carrying out addition condensation of the norbornene derivative is proposed in recent years (JP,4-63807,A, JP,8-198919,A, the Patent Publication Heisei No. 508649 [nine to] gazette, the Patent Publication Heisei No. 505880 [11 to] gazette, etc.). This cyclic olefin system (**) polymer is excellent in heat resistance and transparency, and useful in an optical material, a semiconductor coating material, adhesives, etc. however -- it is high-heat-resistance resin which has a high glass transition temperature, and it is necessary to make working temperature high inevitably like the ring-opening-polymerization object of the above-mentioned norbornene derivative, -- this sake -- degradation at the time of processing, especially yellowing -- coloring still poses a problem.

EFFECT OF THE INVENTION

[Effect of the Invention]By combining a specific antioxidant with the cyclic olefin system (**) polymer which has a glass transition temperature high enough, the coloring which takes place by oxidation degradation is improved substantially, and the heat resistant resin composition of this invention solves the problem of the yellow discoloration under the severe condition which poses a problem conventionally. by development of this art, the semiconductor encapsulant etc. which have impossible plastic-izing of the glass substrate of TFT liquid crystal, and high heat resistance and transparency in respect of heat resistance become possible by old resin.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]This invention by having been made against the background of the technical problem of the above-mentioned conventional technology, and blending with a cyclic olefin system (**) polymer combining a specific antioxidant, It excels in

heat-resistant degradation nature, and aims at providing liquid crystal substrate material, semiconductor coating material, and the suitable heat resistant resin composition for the adhesives of a lens especially.

MEANS

[Means for Solving the Problem] A cyclic olefin system (**) polymer in which this invention includes a repeating unit (a-1) shown with the (A) following general formula (1), (B) Temperature of the 5% weight loss measured by thermogravimetric analysis (TGA) is an antioxidant which is not less than 250 **, (b-1) It is related with a heat resistant resin composition containing a phenolic antioxidant, the Lynn (b-2) system antioxidant, and (b-3) at least one sort of antioxidants chosen from a group of a sulfur-systems antioxidant.

[0007]

[Formula 3]

[0008] $A^1 - A^4$ show independently a hydrogen atom, the alkyl group of the carbon numbers 1-20, a cycloalkyl group, an aryl group, an alkenyl group, a halogen atom, a halogenated hydrocarbon group, or the polar group expressed with $-(CH_2)_kX$ among a general formula (1), respectively. Here, X is $-C(O)OR^1$ and $-OC(O)R^2$, $R^1 - R^2$ show a hydrogen atom, the alkyl group of the carbon numbers 1-20, an alkenyl group, an aryl group, cycloalkyl groups, and these halogenation groups, and k shows the integer of 0-3. The BINIRIDENIRU group formed in $A^1 - A^4$ by A^1, A^2 or A^3 , and A^4 , The imido group formed by A^1, A^2 and A^1, A^3 or A^3, A^4 , and A^2 and A^4 is also contained. l is an integer of 0 or 1.]

Above A thing including a repeating unit (a-2) further shown in (A) cyclic olefin system (**) polymer with a following general formula (2) is preferred.

[0009]

[Formula 4]

[0010] $B^1 - B^4$ among a general formula (2), respectively independently, A hydrogen atom, the hydrocarbon group of the carbon numbers 1-20, and $-(CR^4R^5)_nSi(OR^3)_mR^{6(3-m)}$, $(CR^4R^5) - Si(R^7R^8)OSi(OR^3)_mR^{6(3-m)}$, -The alkoxy silyl groups expressed with $C(O)O(CH_2)_nSi(OR^3)_mR^{6(3-m)}$, allyloxy silyl groups, or such hydrolysis condensation residue are shown, At least one of $B^1 - B^4$ contains alkoxy silyl groups, allyloxy silyl groups, or such hydrolysis condensation residue. Here, R^3 shows the alkyl group or aryl group of 1-10, and $R^4 - R^8$ show the hydrocarbon

group of a hydrogen atom, a halogen atom, or the carbon numbers 1-20 independently, respectively. As for the integer of 0-3, and n, the integer of 0-5 and r of m are 0 or 1.]

Above-mentioned (A) cyclic olefin system (**) polymers are a repeating unit (a-2) shown by the 50 - 99.9-mol % and above general formula (2) in a repeating unit (a-1) shown by the above-mentioned general formula (1) 50 - 0.1-mol % [(a-1) +(a-2) = 100-mol %] Containing is preferred.

[0011]

[Embodiment of the Invention](A) (A) cyclic olefin system (**) polymer used for cyclic olefin system (**) polymer this invention is a polymer (**) of a cyclic olefin system including the repeating unit (a-1) shown in the above-mentioned general formula (1), and the repeating unit (a-2) further shown in the required ***** above-mentioned general formula (2).

[0012]Here, although 2 and 3 addition structural unit the above-mentioned repeating unit (a-1) is indicated to be to the above-mentioned general formula (1) are mentioned, a little 2 and 7 addition structural units which are shown in a following general formula (3) may be included in the repeating unit (a-1).

[0013]

[Formula 5]

[0014][A¹ - A⁴, and l are the same as that of what is shown in the above-mentioned general formula (1) respectively among a general formula (3).]

[0015]Hereafter, (A) cyclic olefin system (**) polymer used for this invention is explained still more concretely. A repeating unit (a-1) used for (A) cyclic olefin system (**) polymer of this invention can be formed by addition condensation of cyclic olefin (henceforth "specific cyclic olefin (1)") shown in a following general formula (4).

[0016]

[Formula 6]

[0017][A¹ - A⁴, and l are the same as that of what is shown in the above-mentioned general formula (1), respectively among a general formula (4).]

[0018]As an example of such specific cyclic olefin (1), 2-norbornene, 5-methyl-2-norbornene, 5-ethyl-2-norbornene, 5-propyl-2-norbornene, 5-butyl-2-norbornene, 5-pentyl-2-norbornene, 5-hexyl-2-norbornene, 5-heptyl-2-norbornene, 5-octyl-2-norbornene, 5-decyl-2-norbornene, 5-dodecyl-2-norbornene, 5,6-dimethyl- 2-norbornene, 5-methyl, 5-ethyl-2-norbornene, 5-phenyl-2-norbornene, 5-vinyl-2-norbornene, 5-allyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-ethylidene-2-norbornene, 5-cyclohexyl-2-norbornene, 5-fluoro-2-norbornene, 5-chloro-2-

norbornene, and 5-norbornene 2-methyl carboxylic acid, 5-norbornene 2-carboxylic acid ethyl, 5-norbornene 2-carboxylic acid butyl, 2-methyl, 5-norbornene 2-methyl carboxylic acid, 2-methyl, 5-norbornene 2-carboxylic acid ethyl, 2-methyl, 5-norbornene 2-carboxylic acid propyl, 2-methyl, 5-norbornene 2-carboxylic acid butyl, 2-methyl, 5-norbornene 2-carboxylic acid trifluoroethyl, 2-methyl, 5-norbornene 2-yl ethyl acetate, 5 - Spiro [norbornene 2-spiro N-phenylsuccinimide 5-norbornene 2-/ N] - Cyclohexylsuccinimide 5-norbornene 2-spiro N-methylsuccinimide 5-norbornene 2, 3-N-phenyl dicarboxyimide 5-norbornene 2,3-N-cyclohexyl dicarboxyimide acrylic acid 2-methyl-5-norbornene, Methacrylic acid 2-methyl-5-norbornene and 5-norbornene 2,3-dimethyl dicarboxylate, 5-norbornene 2,3-diethyl dicarboxylate, 3-tricyclo [4.3.0.1^{2,5}] Decene, 3, 7-tricyclo [4.3.0.1^{2,5}] Decadiene (dicyclopentadiene) 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] Dodecen, 8-methyl, 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] Dodecen, 8-methyl, 8-carbomethoxy, 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] Dodecen, 8-methyl, 8-ethoxycarbonyl, 3-tetracyclo [4.4.0.1^{2,5}.1^{7,10}] Dodecen etc. can be mentioned.

[0019]A compound shown in the above-mentioned general formula (4) which forms the above-mentioned repeating unit (a-1) can be independent one sort, or can be used combining two or more sorts.

[0020]a rate in all the repeating units of the above-mentioned repeating unit (a-1) -- desirable -- 50-99.9-mol % -- further -- desirable -- 80-99.5-mol % -- especially -- desirable -- 90-98-mol % - it contains. It is it easy to hydrolyze a polymer to be less than [50 mol %], and formation of a film and a sheet becomes difficult. On the other hand, formation of a bridging body becomes difficult at the same time a fall of adhesion to metal substrates, such as a fall of film strength, Si, aluminum, Au, and Cu, etc. will arise, if 99.9-mol % is exceeded.

[0021]a repeating unit (a-2) shown in the above-mentioned general formula (2) -- (**) -- it is formed by carrying out addition copolymerization of the cyclic olefin (henceforth "specific cyclic olefin (2)") shown in a following general formula (5) to specific cyclic olefin (1) of the above-mentioned general formula (4). As other methods, (**) 5-trichlorosilyl 2-norbornene, 5-dichloromethylsilyl 2-norbornene, 5-dichloroethylsilyl 2-norbornene, 5-norbornene 2-carboxylic acid trichlorosilyl propyl, 2-methyl, 5-norbornene 2-carboxylic acid trichlorosilyl propyl, After carrying out addition copolymerization of specific cyclic olefin (3) which has which trichlorosilyl group and a dichloro alkyl silyl group, and the specific cyclic olefin (1), (**-1) By making it react with an alkoxide of a trichlorosilyl group in an obtained copolymer or a dichloro alkyl silyl group, and an alkaline metal, or Ali Loki Cyd of an alkaline metal, It is formed by making it react to alcohol or phenols under existence of an amine compound as other methods (low 2).

[0022]

[Formula 7]

[0023][B¹ - B⁴, and r are the same as that of what is shown in the above-mentioned general formula (2) among a general formula (5).]

[0024]As an example of such specific cyclic olefin (2), 5-trimethoxysilyl 2-norbornene, 5-dimethoxy, chlorosilyl 2-norbornene, 5-methoxy, chloro, methylsilyl 2-norbornene, 5-

dimethoxy, chlorosilyl 2-norbornene, 5-methoxy, a hydride, methylsilyl 2-norbornene, 5-dimethoxy, hydride silyl 2-norbornene, 5-methoxy dimethylsilyl 2-norbornene, 5-triethoxy silyl 2-norbornene, 5-diethoxy, chlorosilyl 2-norbornene, 5-ethoxy, chloro, methylsilyl 2-norbornene, 5-diethoxy, hydride silyl 2-norbornene, 5-ethoxy dimethylsilyl 2-norbornene, 5-ethoxydiethylsilyl 2-norbornene, 5-propoxy dimethylsilyl 2-norbornene, 5-triphenoxy silyl 2-norbornene, 5-diphenoxymethylsilyl 2-norbornene, 5-trimethoxysilyl methyl-2-norbornene, 5-(2-trimethoxysilyl) ethyl-2-norbornene, 5-(2-dimethoxy, chlorosilyl) ethyl-2-norbornene, 5-(1-trimethoxysilyl) ethyl-2-norbornene, 5-(2-trimethoxysilyl) propyl-2-norbornene, 5-(1-trimethoxysilyl) propyl-2-norbornene, 5-triethoxy silyl ethyl-2-norbornene, 5-dimethoxymethylsilylmethyl-2-norbornene, 5-trimethoxy propylsilyl 2-norbornene, 5-norbornene 2-carboxylic acid trimethoxysilylpropyl, 5-norbornene 2-carboxylic acid triethoxy silyl propyl, 5-norbornene 2-carboxylic acid dimethoxy, methylsilylpropyl, 2-methyl, 5-norbornene 2-carboxylic acid trimethoxysilylpropyl, 2-methyl, 5-norbornene 2-carboxylic acid dimethoxy, methylpropyl, 2-methyl, 5-norbornene 2-carboxylic acid triethoxy silyl propyl, etc. are mentioned.

[0025] By a repeating unit (a-2) being included at a moderate rate in a cyclic olefin system (**) polymer of this invention, while adhesion and adhesion to metal are improved, material which was excellent in solvent resistance by hydrolysis and crosslinking reaction can be obtained. a rate in all the repeating units of the above-mentioned repeating unit (a-2) -- desirable -- 0.1-50-mol % -- further -- desirable -- 0.5-20-mol % -- it is 2-10-mol % especially preferably. Less than [0.1 mol %], the content becomes insufficient [the above-mentioned effect]. On the other hand, if 50-mol % is exceeded, by alkoxy silyl groups which exists superfluously in a cyclic olefin system (**) polymer, allyloxy silyl groups, or such hydrolysis condensation residue. (**) It is easy to hydrolyze a polymer, and preservation stability will become bad, and it will not become what has the smooth surface of a sheet film.

[0026] A polymerization method of specific cyclic olefin (1) of this invention or a copolymerization method of cyclic olefin (1) and cyclic olefin (2) is performed by a following method. As a polymerization catalyst, a catalyst which forms a cation complex or cation complexes, such as periodic table 8 fellows' nickel, Pd, and Co, is usually used. As a typical thing, $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$, $[\text{Pd}(\text{PhCN})_4][\text{SbF}_6]_2$, Di-mu-chloro-screw (bicyclo [6-methoxy]) [2.2.1] Hept 2-ene- and 5sigma, 2piPd (it abbreviates to "I" hereafter.), I, methylalumoxane (it abbreviates to MAO hereafter) and I, AgSbF_6 and I, and AgBF_4 , $[(\eta^3\text{-aryl})\text{PdCl}]_2$ and AgSbF_6 , $[(\eta^3\text{-aryl})\text{PdCl}]_2$ and AgBF_4 , $[(\eta^3\text{-clo chill})\text{Pd}(\text{cyclo-octadiene})][\text{PF}_6]^{**}$, $[(1, 5\text{-cyclo-octadiene})\text{Pd}(\text{Cl})(\text{CH}_3)]\text{PPh}_3$ and NaB [3, 5-(CF_3) $_2\text{C}_6\text{H}_3$] $_4$, $[(\eta^3\text{-clo chill})\text{nickel}(\text{cyclo-octadiene})][\text{B}(\text{CF}_3)_2(\text{C}_6\text{H}_4)_4]^{**}$, $[\text{NiBr}(\text{NPMMe}_3)]_4$, MAO and nickel(octoate) $_2$, MAO and nickel(octoate) $_2$, $\text{B}(\text{C}_6\text{F}_5)_3$, and AlEt_3 , nickel(octoate) $_2$, a reactant of HSbF_6 , BF_3 and Et_2O , and AlEt_3 , A reactant of nickel(octoate) $_2$, a reactant of HSbF_6 , BF_3 and Et_2O , and AlEt_3 , nickel(octoate) $_2$, a reactant of HSbF_6 , and AlEt_2F , A reactant and AlEtF_2 of nickel(octoate) $_2$ and HSbF_6 , nickel(naphthoate) $_2$, a reactant of HSbF_6 , BF_3 and Et_2O , and AlBu_3 , A reactant of nickel(naphthoate) $_2$, a reactant of HSbF_6 , $\text{B}(\text{C}_6\text{F}_5)_3$, and AlEt_3 , nickel(octoate) $_2$, $\text{Ph}_3\text{C-B}(\text{C}_6\text{F}_5)_3$, AlEt_3 , Toluene-nickel(C_6F_5) $_2$, Xylene-nickel(C_6F_5) $_2$, Mesitylene-nickel(C_6F_5) $_2$, Co (neo decanoate), MAO, etc. are mentioned.

[0027] As a solvent, alicyclic hydrocarbon solvents, such as cyclohexane, cyclopentane, and methylcyclopentane, Aliphatic hydrocarbon solvents, such as pentane, hexane, heptane, and octane, Aromatic hydrocarbon solvents, such as toluene, benzene, and xylene, dichloromethane, Halogenated hydrocarbon solvents, such as 1,2-dichloroethylene and chlorobenzene, Ethyl

acetate, butyl acetate, gamma-butyrolactone, propylene glycol, A solvent chosen from polar solvents, such as wood ether, nitromethane, N-methyl pyrrolidone, pyridine, N,N'-dimethylimidazolidinone, dimethylformamide, and an acetamide, etc. is used.

[0028] As the method of a polymerization, under nitrogen or argon atmosphere, a monomer and a molecular weight modifier which become a reaction vessel from a solvent and cyclic olefin are taught, and a polymerization system is set as temperature of the range of -20 to 100 **. Next, the above-mentioned catalyst component is added and it polymerizes in -20 to 100 **. A weight ratio of a solvent/monomer is performed in 1-20. Regulation of a molecular weight is adjusted by the target molecular weight with an inversion rate and polymerization temperature to quantity of a polymerization catalyst, an addition of molecular weight modifiers, such as alpha olefin, hydrogen, and a diphenyl dihydrosilane, and a polymer (**). A stop of a polymerization is performed by water, alcohol, organic acid, carbon dioxide, etc. (**) The water/alcoholic mixture of acid chosen as a polymer solution from maleic acid, fumaric acid, and oxalic acid are added, and a catalyst residue is separated and removed from a polymer solution (**). (**) A polymer is obtained by putting a polymer solution (**) in alcohol chosen from methanol, ethanol, isopropanol, etc., solidifying it, and carrying out reduced pressure drying. At this process, an unreacted monomer which remains in a polymer solution (**) is also removed.

[0029] A molecular weight of (A) cyclic olefin system (**) polymer used for this invention, By polystyrene conversion measured by gel permeation chromatogram used as a solvent, o-dichlorobenzene. It is desirable and a number average molecular weight is [5,000-1,000,000, and weight average molecular weight] preferred to 10,000-1,500,000, and a pan, a number average molecular weight is 10,000 to 700,000, and weight average molecular weight is 20,000-1,000,000. Disruptive strength when a number average molecular weight uses less than 5,000 and weight average molecular weight considers it as a film, a thin film, and a sheet by less than 10,000 becomes insufficient in many cases. On the other hand, if a number average molecular weight exceeds 1,000,000 and weight average molecular weight exceeds 1,500,000, Since a problem of insoluble matter to a cast solvent in which the molding workability of a sheet obtained and a film falls, and solution viscosity becomes high at the time of cast film film production increasing arises, handling becomes difficult.

[0030] 150 ** - 400 ** of glass transition temperature [250-380 ** of / 270-370 ** of] of (A) cyclic olefin system (**) polymer of this invention is 300-350 ** especially preferably still more preferably preferably. Here, glass transition temperature of (A) cyclic olefin system (**) polymer of this invention is called for with peak temperature of temperature distribution of T_{Δ} measured by dynamic viscoelasticity. ($\text{Storage-modulus } E'$, $\text{loss-modulus } E''$ ($T_{\Delta} = E''/E'$)) Less than 150 ** of heat resistance is [the glass transition temperature] insufficient, and if glass transition temperature exceeds 400 ** on the other hand, problems, like film body formation which breaks easily becomes difficult will arise.

[0031] (B) An antioxidant, next the (B) antioxidant used for a heat-resistant constituent of this invention are at least one sort chosen from a group of a phenolic antioxidant (b-1), the Lynn (b-2) system antioxidant, and (b-3) a thioether series antioxidant.

[0032] (b-1) Phenolic antioxidant; (b-1) it is the feature that an alkyl group which has a straight chain or branching ($C_1 - C_{20}$) has replaced a phenolic antioxidant by the 2nd place of a phenolic group and/or the 6th place. As an example of (b-1), it is pentaerythrityl tetrakis. [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] 3,9-screw {2 - [3-(3-t-butyl-4-hydroxy-5-methylphenyl) propionyloxy] -1,1-dimethylethyl}2, 4 and 8, 10-tetraoxaspiro [5, 5] An undecane, octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, 1,6-hexane *****-***** [3-(3,5-di-t-butyl-4-

hydroxyphenyl) propionate] 1,3,5-trimethyl 2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) benzene, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-t-butyl-4-ethylphenol, 2,6-diphenyl-4-octadecyloxyphenol, stearyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate, distearyl (3,5-di-t-butyl-4-hydroxybenzyl) phosphonate, a thiodiethylene glycol screw [(3,5-di-t-butyl-4-hydroxyphenyl) Propionate] A 4,4'-thioscrew (6-t-butyl-m-cresol), 2-octylthio 4,6-JI (3,5-di-t-butyl-4-hydroxyphenoxy)-s-triazine, 2,2'-methylenebis (4-methyl-6-t-butyl-6-butylphenol), 2, - 2'-methylenebis (4-ethyl-6-t-butylphenol), a screw [3,3-bis(4-hydroxy-3-t-butylphenyl)butyric acid] Glycol ester, 4,4'-butylidenebis (6-t-butyl-m-cresol), A 2,2'-ethylidenescrew (4,6-di-t-butylphenol), a 2,2'-ethylidenescrew (4-s-butyl-6-t-butylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, a screw [2-t-butyl-4-methyl-6-(2-hydroxy-3-t-butyl-5-methylbenzyl) phenyl] Terephthalate; 1,3,5-tris (2,6-dimethyl- 3-hydroxy-4-t-butylbenzyl) isocyanurate, 1,3,5-tris (3,5-di-t-butyl-4-hydroxybenzyl)-2,4,6-trimethyl benzene, 1 and 3, 5-tris [(3,5-di-t-butyl-4-hydroxyphenyl) Propionyloxy ethyl] Isocyanurate, tetrakis [Methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] Methane, 2-t-butyl-4-methyl-6-(2-acryloyloxy 3-t-butyl-5-methylbenzyl) phenol, a 3,9-bis(1,1-dimethyl- 2-hydroxyethyl)-2,4,8,10-tetraoxaspiro [5, 5] undecane-screw [beta-(3-t-butyl-4-hydroxy-5-methylphenyl) propionate] Triethylene glycol screw [beta-(3-t-butyl-4-hydroxy-5-methylphenyl) propionate] 1,1'-bis(4-hydroxyphenyl)cyclohexane, 2,2'-methylenebis (4-methyl 6-t-butylphenol), 2,2' **MECHIREMBISU (4-ethyl 6-t-butylphenol), 2,2' **MECHIREMBISU (6-(1-methylcyclohexyl)-4-methyl phenol), 4,4' **BUCHIRIDEMBISU (3-methyl 6-t-butylphenol), 3,9-screw (2-(3-t-butyl 4-hydroxy 5-methylphenyl PUROPIONIROKISHI) 1,1 **JIME chill ethyl) - 2, 4 and 8, 10 **TETORA oxaspiro (5, 5) undecane, 4,4'-thiobis(3-methyl-6-t-butylphenol), 4,4' **BISU (3,5 **JI t-butyl 4-hydroxybenzyl) sulfide, 4,4' **CHIOBISU (6-t-butyl 2-methyl phenol), 2,5-di-t-butylhydroquinone, 2,5-G t-amyl hydroquinone and 2-t-butyl 6-(3-t-butyl 2-hydroxy 5-methylbenzyl)-4-methylphenyl acrylate and 2,4-dimethyl 6- (1-methylcyclohexyl and SUCHIRENEITIDDO phenol.) 2,4-bis(octylthio)(methyl)-5-methyl phenol etc. are mentioned. In these, a hindered phenolic antioxidant is preferred.

[0033](b-2) Lynn system antioxidant; (b-2) the Lynn system antioxidant is phosphate which is phosphorus compounds of III value, or phosphate. As an example, bis-(2,6-di-t-butyl-4-methylphenyl)penta pentaerythritoldiphosphite, Tris (2,4-di-t-butylphenyl phosphite), tetrakis (2,4-G t-butyl 5-methylphenyl) - 4 and 4' **BIFENI range phospho night, 3,5-di-t-butyl-4-hydroxybenzyl phosphonate diethyl ester, Bis-(2,6-JIKUMIRU phenyl)pentaerythritoldiphosphite, 2,2-methylene bis(4,6-di-t-butylphenyl)octyl phosphite, Tris (mixed mono- and di-nonylphenyl phosphite), Bis(2,4-di-tert-butylphenyl) penta pentaerythritol di-phosphite, Bis(2,6-di-t-butyl-4-carbomethoxyethyl-phenyl)pentaerythritoldiphosphite, bis(2,6-di-t-butyl-4-octadecyl oxycarbonyl ethyl-phenyl)pentaerythritoldiphosphite, etc. are mentioned. In these, phosphite and phosphate are preferred.

[0034]Thioether series antioxidant; (b-3) (b-3) As an example of a thioether series antioxidant, Dilauryl 3,3'-thiodipropionate, a bis(2-methyl 4-(3-n-dodecyl) thio propionyloxy)-5-t-butylphenyl sulfide, The distearyl 3, 3'-thiodipropionate, pentaerythritol tetrakis (3-lauryl) thiopropionate, etc. are mentioned.

[0035](B) Although an antioxidant is independent or the above-mentioned (b-1) phenolic antioxidant, the Lynn (b-2) system antioxidant, and a thioether series (b-3) antioxidant can be used together and used for it, respectively, An ingredient (b-1), (b-2), or (b-3) two or more sorts of concomitant use systems of an ingredient are preferably preferred. Not less than 250 ** is required for temperature of a decrease of 5% weight in thermogravimetric analysis (TGA) of

these antioxidants, and it is preferred. [of not less than 300 more **] That whose temperature of a decrease of 5% weight is less than 250 ** will volatilize, when polymer is used at a not less than 150 ** elevated temperature, and an effect of an antioxidant of it will be lost.

[0036]The (B) ingredient of a using rate of (A) cyclic olefin system (**) polymer and the (B) antioxidant in a heat resistant resin composition of this invention is usually 0.3 - 3 weight section preferably 0.05 to 5 weight section to (A) ingredient 100 weight section. (B) If a using rate of an ingredient cannot acquire oxidation degradation preventive effect sufficient in less than 0.05 weight section but adds exceeding five weight sections on the other hand, deterioration of quality of a mechanical strength of a constituent obtained, glass transition temperature, etc., an increase in a volatile constituent at the time of heating, etc. arise, and it is not desirable.

[0037](A) As a method of adding these (B) antioxidants to a cyclic olefin system (**) polymer, How to add at the time of specific cyclic olefin (1), composition of (2), or refining, A method of adding to a cyclic olefin system (**) polymer solution, a method of adding at the time of refining of a ** (**) polymer, etc. are mentioned, and except adding to the polymer (**) itself, it can also add to a solvent etc. beforehand and is not limited in particular to them.

[0038]A norbornene system polymer and an addition polymer which are the hydrides of a ring-opening-polymerization object conventionally publicly known to (A) cyclic olefin system (**) polymer of this invention [For example, JP,61-29260,A, JP,60-16870,A, JP,60-26024,A, JP,2-51511,A, JP,1-132625,A, A polymer of statements, such as JP,1-132626,A, JP,4-202404,A, JP,4-63807,A, JP,8-198919,A, the Patent Publication Heisei No. 508649 [nine to] gazette, the Patent Publication Heisei No. 505880 [11 to] gazette, and JP,61-292601,A,] (**) Heat resistance and an optical property (transparency, low birefringence) excellent in a constituent produced by blending, and adhesion and adhesion can be given.

[0039]In such a constituent, although a blending ratio of (A) cyclic olefin system (**) polymer of this invention and other polymers is suitably chosen according to a kind of a polymer (**) of this invention, and other polymers, both compatibility, and the purpose of using a constituent, In order to obtain a constituent which has the outstanding heat resistance, a rate of (A) cyclic olefin system (**) polymer of this invention is 20 to 80 % of the weight especially preferably ten to 90% of the weight still more preferably five to 95% of the weight preferably.

[0040]moreover -- a heat resistant resin composition of this invention -- in addition, a range which does not spoil heat resistance for stabilizer which is effective in preventing degradation of resin by light -- one sort -- or two or more sorts may be combined and it may use. As an ultraviolet ray absorbent, a benzophenone series, a salicylate series, a benzotriazol system, etc. are mentioned among what is used as stabilizer. Below, an example of stabilizer is listed.

[0041]As amine system stabilizer, phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, Dioctyl phenylamine, N,N'-diphenyl-p-phenylenediamine, N' and N'-di-beta-naphthyl p-phenylene diamine, N-cyclohexyl-N'-phenyl-p-phenylene diamine, a 2-(3,5-t-butyl-4-hydroxybenzyl)-2-n-butylmalonic acid screw (1,2,2,6,6-pentamethyl 4-piperidyl) and poly -- { [6-(1,1,3,3-tetramethylbutyl) imino-1,3,5-triazine 2,4-diyl] [(2, 2, 6, and 6-tetramethyl 4-piperidyl) Imino] Hexamethylene[(2, 2, 6, and 6-tetramethyl 4-piperidyl) Imino] }, a succinate dimethyl 1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine polycondensation thing, bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)sebacate, etc. are mentioned.

[0042]As benzophenone series stabilizer, 2-hydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2,4-dihydroxybenzophenone, 2,2', 4-trihydroxy benzophenone, 2,2', and 4,4'-tetrahydroxybenzophenone etc. are mentioned.

[0043]As salicylate series stabilizer, phenyl salicylate and 2,4-di-t-buthylphenyl 3' and 5'-di-t-

butyl-4'-hydroxy benzoate, Phenyl-3,5-di-t-butyl-4-hydroxy benzoate and 2-methyl-4-t-buthylphenyl 3' and 5'-di-t-butyl-4'-hydroxy benzoate etc. are mentioned. [0044]As benzotriazol system stabilizer, 2-(2'-hydroxy-5'-methylphenyl) benzotriazol, A 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-t-buthylphenyl) benzotriazol, 2-(2'-hydroxy-5'-t-octylphenyl) benzotriazol, 2-(2'-3' and 5'-di-t-amyl phenyl) benzotriazol, etc. are mentioned.

[0045]As hydrazine system stabilizer, they are maleic hydrazide and a N,N'-screw. [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionyl] Hydrazine, N-salicyloyl N'-aldehyde hydrazine, etc. are mentioned.

[0046]As epoxy system stabilizer, epoxidation linseed oil, epoxidized soybean oil, epoxy butyl stearate, epoxy octyl stearate, epoxy lauryl stearate, a low-molecular-weight epoxy resin, etc. are mentioned. each above stabilizer -- one sort -- or two or more sorts are mixed and it is used.

[0047]In a heat resistant resin composition of this invention, if needed further High-class dicarboxylic acid metal salt, Lubricant, such as high-class carboxylate, a plasticizer, a spray for preventing static electricity, inorganic matter and organic system colorant, a foaming agent, inorganic matter and an organic system bulking agent, fire retardant other than the above, a surface gloss improving agent, a flattening, etc. can be added. These various additive agents can be added in a manufacturing process of a resin composition.

[0048]A heat resistant resin composition of this invention is obtained by mixing in a solvent (A) cyclic olefin system (**) polymer and the above-mentioned (B) antioxidant, and an additive agent used further if needed at the time of casting. As a casting solvent, what both (A) and (B) dissolve is preferred.

[0049]Although a heat resistant resin composition of this invention can be used alone, Glass fiber, a metal fiber since compatibility with various polar materials is good, It can also be used as composite materials, such as carbon fiber or these powder, calcium carbonate, talc, gypsum, alumina, silica, mica, CHITSU-ized boron, zirconia, silicon carbide, and potassium titanate.

[0050]A cyclic olefin system copolymer of this invention and a heat resistant resin composition of an antioxidant are suitable for plastic alternate material etc. of a use as which high heat resistance is required, for example, liquid crystal substrate glass. That is, heat resistance required of a substrate material can be satisfied at processes, such as exposure by TFT (thin film transistor) formation of a up to [a liquid crystal display substrate], development, and etching. Since a heat resistant resin composition of this invention has outstanding optical transparency, heat resistance, adhesion and adhesion, and moisture absorption resistance, It is used for electronic parts, such as a light guide plate, a polarization film, a liquid crystal panel, a phase difference film, a transparent conductive film, an OHP film, an optical disc, an optical fiber, and a lens, a medical care container, a container, etc.

[Translation done.] **EXAMPLE**

[Example]Although an example is given and this invention is explained still more concretely hereafter, this invention is not limited to the following examples. Among an example, a part and especially % are weight references, unless it refuses. The weight average molecular weight and the number average molecular weight in an example, intrinsic viscosity, and hue are measured as follows.

It measured at 120 °C by using o-dichlorobenzene as a solvent using H type column by TOSOH CORP. with weight average molecular weight and the product made by number average molecular weight Waters (WATERS), and C [150] type gel-permeation-chromatography device. The obtained molecular weight is a standard polystyrene reduced property.

Various antioxidants were added to the polymer solution at the time of the cast, and the film was created by the cast method using the homogeneous solution. The obtained sample was used as the methylene chloride solution 15%, respectively, and the degree of yellow (YI value) was measured by the transmitted light according to JIS K7103.

[0052] It taught as synthetic example 1 monomer by 5-n-hexyl-2-norbornene 93.75 millimol, 2-norbornene 500 millimol, and 5-triethoxy silyl 2-norbornene 31.25 millimol, and 500 g of toluene was taught to the reactor with a capacity of 1 l. under nitrogen as a solvent. Adjust the system of reaction at 10 °C, and Triethylaluminum 0.5 millimol, Boron trifluoride and diethylether (BF₃ and Et₂O) 0.4 millimol, It added to ****, 0.2 millimols of nickel compounds to which octanoic acid nickel and antimony hexafluoride acid (HSbF₆) were made to react by the mole ratio 1:1 at -15 °C beforehand finally were added with the nickel atom, and the polymerization was started. The polymerization was performed at 30 °C for 2 hours, and the polymerization was suspended by ethanol. The inversion rate to the copolymer was 89%. Lactic acid 60 millimol was added to this copolymer solution, and it was made to react to a catalyst component. The copolymer solution was put into 5 l. of isopropanol, the copolymer was solidified, and the unreacted monomer, the above-mentioned reaction reagent, and the catalyst residue were removed from the copolymer. The solidified copolymer was dried and the copolymer A was obtained. The content of the structural unit containing the triethoxy silyl group in A was 4.9-mol % from 270 MHz and ¹H-NMR analysis (4 ppm ETOKI silyl group methylene absorption, solvent: D₂-toluene, TMS standard). The content of the structural unit originating in 5-n-hexyl-2-norbornene was 14.0-mol % from the analytical curve by the characteristic absorption of 721 cm⁻¹ of infrared analysis. The number average molecular weight of polystyrene conversion of measurement of GPC to the copolymer A was 200,000, and weight average molecular weight was 440,000.

[0053] In the example 1 of synthetic example 2 composition, except using 5-n-hexyl-2-norbornene 125 millimol and 2-norbornene 500 millimol, it carried out like the synthetic example 1 and the copolymer B was obtained. The inversion rate to the copolymer was 92%. The content of the structural unit originating in 5-n-hexyl-2-norbornene was 19.0-mol % from the analytical curve by the characteristic absorption of 721 cm⁻¹ of infrared analysis. The number average molecular weight of polystyrene conversion of the copolymer B was 117,000, and weight average molecular weight was 270,000.

[0054] It is 5-n-hexyl-2-norbornene 93.75 millimol, 2-norbornene 500 millimol, 8-methyl, and 8-carbomethoxy-3-tetracyclo as synthetic example 3 monomer. [4.4.0.1^{2,5}1^{7,10}] Except using dodecen 31.25 millimol, it carried out like the synthetic example 1 and the copolymer C was obtained. The inversion rate to the copolymer was 75%. 8-methyl in C, 8-carbomethoxy-3-tetracyclo [4.4.0.1^{2,5}1^{7,10}] The percentage of the structure originating in dodecen was 4.9-mol % from the analytical curve by the characteristic absorption of infrared analysis 1730 cm⁻¹. The content of the structure originating in 5-n-hexyl-2-norbornene was 14.5-mol % from the analytical curve by the characteristic absorption of 721-cm⁻¹ of infrared analysis. 158, 000, and the weight average molecular weight of the number average molecular weight of polystyrene conversion of C were 300,000.

[0055] Except using 5-n-hexyl-2-norbornene 93.75 millimol, 2-norbornene 500 millimol, and 5-

ethylidene 2-norbornene 31.25 millimol as synthetic example 4 monomer, it carried out like the synthetic example 1 and the copolymer D was obtained. The inversion rate to the copolymer D was 80%. The percentage of the structure unit originating in the 5-ethylidene 2-norbornene in D was 4.9-mol % by the iodination titrimetric method. The content of the structure originating in 5-n-hexyl-2-norbornene was 14.0-mol % from the analytical curve by the characteristic absorption of 721-cm^{-1} of infrared analysis. The number average molecular weight of the copolymer D was 138,000, and weight average molecular weight was 290,000.

[0056]The cyclic olefin system copolymer obtained in example of film production above-mentioned each synthetic example by the cast method was dissolved in toluene, and it prepared so that it might become TSC = 10%. kind antioxidant after filtrating this solution with the filter of a 1-micrometer mesh (b-1) (b-2) -- and -- (b-3) the following table 1 shows -- quantity addition was carried out and it was considered as the homogeneous solution. After applying this on a stainless steel board, the solvent was made to evaporate under a room temperature. The solvent which remains in a film by heat-treating the obtained film at 210 ** under a vacuum for 2 hours was made to evaporate thoroughly, and the target bright film was obtained.

[0057]Example The bright film obtained by 1-23, the comparative example 1 - the 3 above-mentioned cast method was heated in the air, and change of hue (YI value) estimated anti-oxidation degradation nature. Tables 2-5 (b-2) (b-3) The details of various antioxidants used in inside (b-1) are as follows.

(b-1) ingredient; Phenolic antioxidant a: . Pentaerythrityl tetrakis [3-. 3. The 5-di-t-butyl-4-hydroxyphenyl propionate b:1, 3, 5-trimethyl 2 and 4, 6-tris. (3,5-di-t-butyl-4-hydroxybenzyl) benzene c:octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate d:2,6-di-tert-butyl-4-methylphenol (b-2) ingredient; -- Lynn system antioxidant e: . A screw. 2. the 6-di- t - butyl-4-methylphenyl pentaerythritol di-phosphite f:tetrakis (2,4-di-t-butyl-5-methylphenyl)-4,4'-biphenylene diphosphonate g: -- tris (2,4-di-t-buthylphenyl) Phosphite h: . 2,2-methylene-bis(4,6-di-t-butylphenyl)octyl-phosphite (b-3) ingredient; thioether series antioxidant i:bis(2-methyl-4-(3-n-dodecyl) thio propionyloxy)-5-t-buthylphenyl sulfide [0058]

[Table 1]

[0059]

[Table 2]

[0060]
[Table 3]

[0061]
[Table 4]

[0062]
[Table 5]

[Translation done.]

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(54) 【発明の名称】 耐熱性樹脂組成物

(57) 【要約】

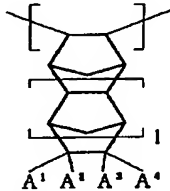
【課題】 環状オレフィン系 (共) 重合体に、特定の酸化防止剤を組み合わせることで、耐熱劣化性に優れ、特に液晶基盤材料や半導体コーティング材料、レンズの接着剤に好適な耐熱性樹脂組成物を提供すること。

【解決手段】 特定の(A)環状オレフィン系 (共) 重合体と、(B) (b-1) フェノール系酸化防止剤、(b-2) リン系酸化防止剤および (b-3) チオエーテル系酸化防止剤の群から選ばれた少なくとも1種の酸化防止剤とを含有する耐熱性樹脂組成物。

【特許請求の範囲】

【請求項1】 (A)下記一般式(1)で示される繰り返し単位(a-1)を含む環状オレフィン系(共)重合体と、(B)熱重量分析(TGA)で測定される5%重量減少の温度が250℃以上である酸化防止剤であって、(b-1)フェノール系酸化防止剤、(b-2)リン系酸化防止剤、および(b-3)硫黄系酸化防止剤の群から選ばれた少なくとも1種の酸化防止剤を含有する耐熱性樹脂組成物。

【化1】

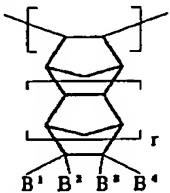


..... (1)

【一般式(1)中、A¹~A⁴はそれぞれ独立して、水素原子、炭素数1~20のアルキル基、シクロアルキル基、アリール基、アルケニル基、ハロゲン原子、ハロゲン化炭化水素基、または-(CH₂)ₖXで表される極性基を示す。ここで、Xは-C(O)OR¹、-OC(O)R¹であり、R¹~R²は水素原子、炭素数1~20のアルキル基、アルケニル基、アリール基、シクロアルキル基およびこれらのハロゲン置換基、kは0~3の整数を示す。また、A¹~A⁴には、A¹とA²またはA³とA⁴で形成されるビニリデン基、A¹とA²、A¹とA³またはA¹とA⁴、A²とA³で形成されるイミド基も含まれる。lは0または1の整数である。】

【請求項2】 上記(A)環状オレフィン系(共)重合体が、さらに下記一般式(2)で示される繰り返し単位(a-2)を含む請求項1記載の耐熱性樹脂組成物。

【化2】



..... (2)

【一般式(2)中、B¹~B⁴はそれぞれ独立して、水素原子、炭素数1~20の炭化水素基、および-(CR¹R²)ₘSi(OR³)ₙR⁴、-(CR¹R²)Si(R¹R²)OSi(OR³)ₙR⁴、-C(O)O(CH₂)ₘSi(OR³)ₙR⁴で表されるアルコキシシリル基もしくはアリロキシシリル基またはこれらの加水分解・縮合残基を示し、B¹~B⁴の少なくとも一つは、アルコキシシリル基もしくはアリロキシシリル基またはこれらの加水分解・縮合残基を含む。ここで、R¹は1~10のアルキル基またはアリール基を示し、R²~R⁴はそれぞれ独立して、水素原子、ハロゲン原子または炭素数1~20の炭化水素基を示す。mは0~3の

整数、nは0~5の整数、rは0または1である。】

【請求項3】 上記請求項1あるいは請求項2に記載の(A)環状オレフィン系(共)重合体と、(B)熱重量分析(TGA)で測定される5%重量減少の温度が250℃以上である酸化防止剤であって、(b-1)ヒンダードフェノール系酸化防止剤、(b-2)ホスファイトおよび/またはホスフェイトからなるリン系酸化防止剤、ならびに(b-3)チオエーテル系酸化防止剤の群から選ばれた少なくとも1種の酸化防止剤を含有する耐熱性樹脂組成物。

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【請求項4】 上記(A)環状オレフィン系(共)重合体が、上記一般式(1)で示される繰り返し単位(a-1)を50~99.9モル%、上記一般式(2)で示される繰り返し単位(a-2)を50~0.1モル%[(a-1)+(a-2)=100モル%]含む請求項1~3いずれか1項記載の耐熱性樹脂組成物。

【請求項5】 上記(B)酸化防止剤の5%重量減少の温度が300℃以上である、請求項1~4いずれか1項記載の耐熱性樹脂組成物。

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【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、特定の環状オレフィン系(共)重合体に、特定の酸化防止剤を組み合わせて配合した耐熱性に優れた樹脂組成物に関する。

【0002】

【従来の技術】従来、透明樹脂としては、ポリメチルメタクリレート、ポリカーボネート、ポリスチレン、3-メチルペンテン樹脂などが知られている。これらの樹脂は、工業的にも大量に製造され、その良好な透明性を生かし、各分野で大量に使用されている。しかしながら、これらの樹脂は、耐熱性が必ずしも充分ではなく、例えば上記樹脂のうち一番耐熱性の高い樹脂とされるポリカーボネートでも、その耐熱性の指標であるガラス転移温度は150℃程度であり、より高い耐熱性を持つ樹脂の開発が望まれている。

【0003】透明性に優れ、より高い耐熱性を持つ樹脂として、極性置換基を有するノルボルネン誘導体の開環重合体が提案されている。しかしながら、ノルボルネン誘導体の開環重合体は、その主鎖に炭素-炭素二重結合を持つため、高温下での酸化劣化が激しく、高いガラス転移温度を持つに係わらず、耐熱性ポリマーとしては実用化されていなかった。このため、上記開環重合体水を水添することにより、その酸化劣化性を改良する試みが提案されている(特公昭57-8815号公報)。この水添による酸化劣化性の改良は、従来の未水添重合体に比べ、その耐酸化劣化性を大幅に向上させることができるが、高いガラス転移温度を持つ高耐熱性樹脂の場合、必然的に加工温度を高くする必要があり、このため加工時の劣化、特に黄変着色が依然として問題となっている。

【0004】また、近年、ノルボルネン誘導体を付加重

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合して得られる環状オレフィン系(共)重合体が提案されている(特開平4-63807号公報、特開平8-198919号公報、特表平9-508649号公報、特表平11-505880号公報など)。この環状オレフィン系(共)重合体は、耐熱性、透明性に優れ、光学材料や半導体コーティング材、接着剤などに有用である。しかしながら、上記のノルボルネン誘導体の開環重合体と同様に、高いガラス転移温度を有する高耐熱性樹脂であり、必然的に加工温度を高くする必要があり、このため加工時の劣化、特に黄変着色が依然として問題となっている。

【0005】

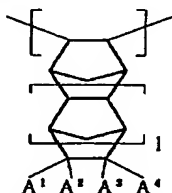
【発明が解決しようとする課題】本発明は、上記従来技術の課題を背景になされたもので、環状オレフィン系(共)重合体に、特定の酸化防止剤を組み合わせて配合することにより、耐熱劣化性に優れ、特に液晶基板材料や半導体コーティング材料、レンズの接着剤に好適な耐熱性樹脂組成物を提供することを目的とする。

【0006】

【課題を解決するための手段】本発明は、(A)下記一般式(1)で示される繰り返し単位(a-1)を含む環状オレフィン系(共)重合体と、(B)熱重量分析(TGA)で測定される5%重量減少の温度が250℃以上である酸化防止剤であって、(b-1)フェノール系酸化防止剤、(b-2)リン系酸化防止剤、および(b-3)硫黄系酸化防止剤の群から選ばれた少なくとも1種の酸化防止剤を含有する耐熱性樹脂組成物に関する。

【0007】

【化3】



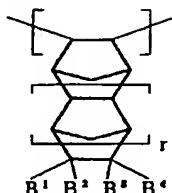
..... (1)

【0008】〔一般式(1)中、A¹~A⁴はそれぞれ独立して、水素原子、炭素数1~20のアルキル基、シクロアルキル基、アリール基、アルケニル基、ハロゲン原子、ハロゲン化炭化水素基、または-(CH₂)ₖXで表される極性基を示す。ここで、Xは-C(O)OR¹、-OC(O)R²であり、R¹~R²は水素原子、炭素数1~20のアルキル基、アルケニル基、アリール基、シクロアルキル基およびこれらのハロゲン置換基、kは0~3の整数を示す。また、A¹~A⁴には、A¹とA²またはA³とA⁴で形成されるビニリデニル基、A¹とA³、A¹とA⁴またはA²とA³、A²とA⁴で形成されるイミド基も含まれる。1は0または1の整数である。〕

上記(A)環状オレフィン系(共)重合体には、さらに下記一般式(2)で示される繰り返し単位(a-2)を含むものが好ましい。

【0009】

【化4】



..... (2)

【0010】〔一般式(2)中、B¹~B⁴はそれぞれ独立して、水素原子、炭素数1~20の炭化水素基、および-(CR¹R²)ₘSi(OR³)ₙR⁴(ₘ₊ₙ=1)、-(CR¹R²)Si(R⁵R⁶)OSi(OR³)ₙR⁴(ₘ₊ₙ=1)、-C(O)O(CH₂)ₖSi(OR³)ₙR⁴(ₘ₊ₙ=1)で表されるアルコキシシリル基もしくはアリロキシシリル基またはこれらの加水分解・縮合残基を示し、B¹~B⁴の少なくとも一つは、アルコキシシリル基もしくはアリロキシシリル基またはこれらの加水分解・縮合残基を含む。ここで、R¹は1~10のアルキル基またはアリール基を示し、R²~R⁶はそれぞれ独立して、水素原子、ハロゲン原子または炭素数1~20の炭化水素基を示す。mは0~3の整数、nは0~5の整数、rは0または1である。〕

さらに、上記(A)環状オレフィン系(共)重合体は、上記一般式(1)で示される繰り返し単位(a-1)を50~99.9モル%、上記一般式(2)で示される繰り返し単位(a-2)を50~0.1モル%〔(a-1)+(a-2)=100モル%〕含むことが好ましい。

【0011】

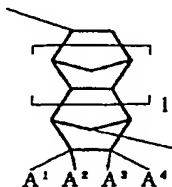
【発明の実施の形態】(A)環状オレフィン系(共)重合体

本発明に用いられる(A)環状オレフィン系(共)重合体は、上記一般式(1)に示す繰り返し単位(a-1)、さらに必要に応じて上記一般式(2)に示す繰り返し単位(a-2)を含む環状オレフィン系の(共)重合体である。

【0012】ここで、上記繰り返し単位(a-1)は、上記一般式(1)に示される2,3付加構造単位が挙げられるが、繰り返し単位(a-1)には、下記一般式(3)に示す2,7付加構造単位が、少量含まれていてもよい。

【0013】

【化5】



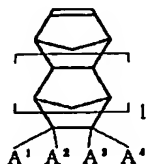
..... (3)

【0014】〔一般式(3)中、A¹~A⁴および1はそれぞれ上記一般式(1)に示すものと同一である。〕

【0015】以下、本発明に用いられる(A)環状オレフィン系(共)重合体について、さらに具体的に説明する。本発明の(A)環状オレフィン系(共)重合体に用いられる繰り返し単位(a-1)は、下記一般式(4)に示す環状オレフィン(以下、「特定の環状オレフィン(1)」という。)の付加重合により形成することができる。

【0016】

【化6】



..... (4)

【0017】〔一般式(4)中、A¹~A⁴および1は、それぞれ上記一般式(1)に示すものと同一である。〕

【0018】このような特定の環状オレフィン(1)の具体例としては、2-ノルボルネン、5-メチル-2-ノルボルネン、5-エチル-2-ノルボルネン、5-プロピル-2-ノルボルネン、5-ブチル-2-ノルボルネン、5-ペンチル-2-ノルボルネン、5-ヘキシル-2-ノルボルネン、5-ヘプチル-2-ノルボルネン、5-オクチル-2-ノルボルネン、5-デシル-2-ノルボルネン、5-ドデシル-2-ノルボルネン、5,6-ジメチル-2-ノルボルネン、5-メチル、5-エチル-2-ノルボルネン、5-フェニル-2-ノルボルネン、5-ビニル-2-ノルボルネン、5-アリル-2-ノルボルネン、5-イソプロピリデン-2-ノルボルネン、5-エチリデン-2-ノルボルネン、5-シクロヘキシル-2-ノルボルネン、5-フロロ-2-ノルボルネン、5-クロロ-2-ノルボルネン、5-ノルボルネン-2-カルボン酸メチル、5-ノルボルネン-2-カルボン酸エチル、5-ノルボルネン-2-カルボン酸ブチル、2-メチル、5-ノルボルネン-2-カルボン酸メチル、2-メチル、5-ノルボルネン-2-カルボン酸エチル、2-メチル、5-ノルボルネン-2-カルボン酸ブチル、2-メチル、5-ノルボルネン-2-カルボン酸トリフロロエチル、2-メチル、5-ノルボルネン-2-イル酢酸エチル、5-ノルボルネン-2-スビロ-N-フェニルスクシンイミド5-ノルボルネン-2-スビロ-N-シクロヘキシルスクシンイミド5-ノルボルネン-2-スビロ-N-メチルスクシンイミド5-ノルボルネン-2,3-N-フェニルジカルボキシイミド5-ノルボルネン-2,3-N-シクロヘキシルジカルボキシイミドアクリル酸2-メチル-5-ノルボルネン、メタクリル酸2-メチル-5-ノルボルネン、5-ノルボルネン-2,3-ジカルボン酸ジメチル、5-ノルボルネン-2,3-ジカルボン酸ジエチル、

10 5-ノルボルネン-2,3-ジカルボン酸ジエチル、

ル、3-トリシクロ〔4,3,0,1^{2,5}〕デセン、3,7-トリシクロ〔4,3,0,1^{2,5}〕デカジエン(ジシクロペンタジエン)

3-テトラシクロ〔4,4,0,1^{2,5},1^{7,10}〕ドデセン、8-メチル、3-テトラシクロ〔4,4,0,1^{2,5},1^{7,10}〕ドデセン、8-メチル、8-メトキシカルボニル、3-テトラシクロ〔4,4,0,1^{2,5},1^{7,10}〕ドデセン、8-メチル、8-エトキシカルボニル、3-テトラシクロ〔4,4,0,1^{2,5},1^{7,10}〕ドデセン、などを挙げることができる。

【0019】上記繰り返し単位(a-1)を形成する上記一般式(4)に示す化合物は、1種単独または2種以上を組み合わせ用いることができる。

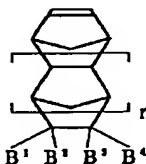
【0020】上記繰り返し単位(a-1)の全繰り返し単位中の割合は、好ましくは50~99.9モル%、さらに好ましくは80~99.5モル%、特に好ましくは90~98モル%含む。50モル%未満であると、重合体が加水分解しやすく、フィルム、シートの形成が困難となる。一方、99.9モル%を超えると、フィルム強度の低下、Si、Al、Au、Cuなどの金属基板への密着性の低下などが生ずると同時に、架橋体の形成が困難となる。

【0021】上記一般式(2)に示す繰り返し単位(a-2)は、

(イ)下記一般式(5)に示す環状オレフィン(以下、「特定の環状オレフィン(2)」という。)を上記一般式(4)の特定の環状オレフィン(1)と付加重合することにより、形成される。(ロ)また、他の方法として、5-トリクロロシリル-2-ノルボルネン、5-ジクロロメチルシリル-2-ノルボルネン、5-ジクロロエチルシリル-2-ノルボルネン、5-ノルボルネン-2-カルボン酸トリクロロシリルプロピル、2-メチル、5-ノルボルネン-2-カルボン酸トリクロロシリルプロピル、などのトリクロロシリル基、ジクロロアルキルシリル基を有する特定の環状オレフィン-(3)と特定の環状オレフィン(1)とを付加重合した後、(ロ-1)得られた共重合体中のトリクロロシリル基またはジクロロアルキルシリル基とアルカリ金属のアルコキシドまたはアルカリ金属のアリロキシドと反応させることにより、また他の方法として(ロ-2)アミン化合物の存在下、アルコールまたはフェノール類と反応させることにより、形成される。

【0022】

【化7】



..... (5)

【0023】〔一般式(5)中、 $B^1 \sim B^4$ および r は、上記一般式(2)に示すものと同一である。〕

【0024】このような特定の環状オレフィン(2)の具体例としては5-トリメトキシシリル-2-ノルボルネン、5-ジメトキシ、クロロシリル-2-ノルボルネン、5-メトキシ、クロロ、メチルシリル-2-ノルボルネン、5-ジメトキシ、クロロシリル-2-ノルボルネン、5-メトキシ、ヒドリド、メチルシリル-2-ノルボルネン、5-ジメトキシ、ヒドリドシリル-2-ノルボルネン、5-メトキシジメチルシリル-2-ノルボルネン、5-トリエトキシシリル-2-ノルボルネン、5-ジエトキシ、クロロシリル-2-ノルボルネン、5-エトキシ、クロロ、メチルシリル-2-ノルボルネン、5-ジエトキシ、ヒドリドシリル-2-ノルボルネン、5-エトキシジメチルシリル-2-ノルボルネン、5-エトキシジエチルシリル-2-ノルボルネン、5-プロポキシジメチルシリル-2-ノルボルネン、5-トリフェノキシシリル-2-ノルボルネン、5-ジフェノキシメチルシリル-2-ノルボルネン、5-トリメトキシシリルメチル-2-ノルボルネン、5-(2-トリメトキシシリル)エチル-2-ノルボルネン、5-(2-ジメトキシ、クロロシリル)エチル-2-ノルボルネン、5-(1-トリメトキシシリル)エチル-2-ノルボルネン、5-(2-トリメトキシシリル)プロピル-2-ノルボルネン、5-(1-トリメトキシシリル)プロピル-2-ノルボルネン、5-トリエトキシシリルエチル-2-ノルボルネン、5-ジメトキシメチルシリルメチル-2-ノルボルネン、5-トリメトキシプロピルシリル-2-ノルボルネン、5-ノルボルネン-2-カルボン酸トリメトキシシリルプロピル、5-ノルボルネン-2-カルボン酸トリエトキシシリルプロピル、5-ノルボルネン-2-カルボン酸ジメトキシ、メチルシリルプロピル、2-メチル、5-ノルボルネン-2-カルボン酸トリメトキシシリルプロピル、2-メチル、5-ノルボルネン-2-カルボン酸ジメトキシ、メチルプロピル、2-メチル、5-ノルボルネン-2-カルボン酸トリエトキシシリルプロピル、などが挙げられる。

【0025】また、本発明の環状オレフィン系(共)重合体中に繰返し単位(a-2)が、適度な割合で含まれることで、金属への接着・密着性が改良されると同時に、加水分解、架橋反応によって耐溶剤性に優れた材料を得ることができる。上記繰返し単位(a-2)の全繰返し単位中の割合は、好ましくは0.1~50モル%、さらに好ましくは0.5~20モル%、特に好ましくは2~10モル%である。その含有量が0.1モル%未満では、上記の効果が不充分となる。一方、50モル%を超えると、環状オレフィン系(共)重合体中に過剰に存在するアルコキシシリル基もしくはアリロキシシリル基またはこれらの加水分解・縮合残基により、(共)重合体が加水分解しやすく、保存安定性が悪いものとな

り、かつシートフィルムの表面が滑らかなものとならない。

【0026】本発明の特定の環状オレフィン(1)の重合方法、あるいは、環状オレフィン(1)と環状オレフィン(2)との共重合方法は、下記の方法によって行われる。重合触媒としては、通常、周期律表8族のNi、Pd、Coなどのカチオン錯体またはカチオン錯体を形成する触媒が用いられる。代表的なものとして、 $[Pd(CH_3CN)_4]$ 、 $[BF_4]$ 、 $[Pd(PhCN)_4]$ 、 $[SbF_6]$ 、ジ-μ-クロロビス(6-メトキシビシクロ[2.2.1]ヘプト-2-エン-エンド-5σ, 2π)Pd(以下、「I」と略す。)、Iとメチルアルモキサン(以下、MAOと略す)、Iと $AgSbF_6$ 、Iと $AgBF_4$ 、 $[(\eta^3\text{-アリール})PdCl]$ 、と $AgSbF_6$ 、 $[(\eta^3\text{-アリール})PdCl]$ 、と $AgBF_4$ 、 $[(\eta^3\text{-クロチル})Pd(\text{シクロオクタジエン})]$ 、 $[PF_6]$ 、 $[(1, 5\text{-シクロオクタジエン})Pd(CH_3)(Cl)]$ と PPh_3 、と $NaB[3, 5-(CF_3)_2C_6H_3]$ 、 $[(\eta^3\text{-クロチル})Ni(\text{シクロオクタジエン})]$ 、 $[B(CF_3)_2(C_6H_5)]$ 、 $[NiBr(NPMe_2)]$ 、とMAO、Ni(オクトエート)、とMAO、Ni(オクトエート)、と $B(C_6F_5)_2$ 、と $AlEt_3$ 、Ni(オクトエート)、と $HSbF_6$ の反応物と $BF_3 \cdot Et_2O$ と $AlEt_3$ 、Ni(オクトエート)、と $HSbF_6$ の反応物と $BF_3 \cdot Et_2O$ と $AlEt_3$ の反応物、Ni(オクトエート)、と $HSbF_6$ の反応物と $AlEt_2F$ 、Ni(オクトエート)、と $HSbF_6$ の反応物と $AlEt_2F$ 、Ni(ナフトエート)、と $HSbF_6$ の反応物と $BF_3 \cdot Et_2O$ と $AlBu_3$ 、Ni(ナフトエート)、と $HSbF_6$ の反応物と $B(C_6F_5)_2$ 、と $AlEt_3$ の反応物、Ni(オクトエート)、と $Ph_3C \cdot B(C_6F_5)_2$ 、と $AlEt_3$ 、 $Toluene \cdot Ni(C_6F_5)_2$ 、 $Xylene \cdot Ni(C_6F_5)_2$ 、 $Mesitylene \cdot Ni(C_6F_5)_2$ 、 Co (ネオデカノエート)とMAO、などが挙げられる。

【0027】溶媒としては、シクロヘキサン、シクロペンタン、メチルシクロペンタンなどの脂環式炭化水素溶媒、ペンタン、ヘキサン、ヘプタン、オクタンなどの脂肪族炭化水素溶媒、トルエン、ベンゼン、キシレンなどの芳香族炭化水素溶媒、ジクロロメタン、1, 2-ジクロロエチレン、クロロベンゼンなどのハロゲン化炭化水素溶媒、酢酸エチル、酢酸ブチル、γ-ブチロラクトン、プロピレングリコール、ジメチルエーテル、ニトロメタン、N-メチルピロリドン、ピリジン、N, N'-ジメチルイミダゾリジノン、ジメチルフォルムアミド、アセトアミドなどの極性溶媒などから選ばれた溶媒が用いられる。

【0028】重合の方法として、窒素またはアルゴン雰

雰囲気下で、反応容器に溶媒と環状オレフィンからなるモノマーと分子量調節剤を仕込み、 -20°C から 100°C の範囲の温度に重合系を設定する。次に、上記触媒成分を添加して、 -20°C から 100°C の範囲で重合を行う。溶媒/モノマーの重量比は、1~20の範囲で行われる。分子量の調節は、重合触媒の量と α -オレフィン、水素、ジフェニルジヒドロシランなどの分子量調節剤の添加量、(共)重合体への転化率および重合温度によって、目的とする分子量に調節される。重合の停止は水、アルコール、有機酸、炭酸ガスなどにより行われる。(共)重合体溶液にマレイン酸、フマル酸、シュウ酸から選ばれた酸の水/アルコール混合物を添加して、触媒残さを(共)重合体溶液から分離・除去する。

(共)重合体は、(共)重合体溶液をメタノール、エタノール、イソプロパノールなどから選ばれたアルコール中に入れて、凝固し、減圧乾燥することにより得られる。この工程で、(共)重合体溶液に残存する未反応モノマーも除去される。

【0029】本発明に用いられる(A)環状オレフィン系(共)重合体の分子量は、 α -ジクロロベンゼンを溶媒とするゲル・パーミエションクロマトグラムで測定されるポリスチレン換算で、好ましくは数平均分子量が5,000~1,000,000、重量平均分子量が10,000~1,500,000、さらに好ましくは、数平均分子量が10,000から700,000、重量平均分子量が20,000~1,000,000である。数平均分子量が5,000未満、重量平均分子量が10,000未満では、フィルム、薄膜、シートとしたときの破壊強度が不十分となることが多い。一方、数平均分子量が1,000,000を超え、重量平均分子量が1,500,000を超えると、得られるシート、フィルムの成形加工性が低下し、また、キャストフィルム製膜時に溶液粘度が高くなる、キャスト溶媒への不溶分が増加するなどの問題点が生ずるため、取扱いが困難となる。

【0030】なお、本発明の(A)環状オレフィン系(共)重合体のガラス転移温度は、 150°C ~ 400°C 、好ましくは 250°C ~ 380°C 、さらに好ましくは 270°C ~ 370°C 、特に好ましくは 300°C ~ 350°C である。ここで、本発明の(A)環状オレフィン系(共)重合体のガラス転移温度は、動的粘弾性で測定される $\text{Tan } \delta$ の温度分散のピーク温度で求められる。(貯蔵弾性率 E' 、損失弾性率 E'' 、($\text{Tan } \delta = E''/E'$)そのガラス転移温度が 150°C 未満では、耐熱性が不十分であり、一方ガラス転移温度が 400°C を超えると、割れやすくなる、フィルム体形成が困難となる、などの問題が生ずる。

【0031】(B)酸化防止剤

次に、本発明の耐熱性組成物に用いられる(B)酸化防止剤は、(b-1)フェノール系酸化防止剤、(b-

2)リン系酸化防止剤および(b-3)チオエーテル系酸化防止剤の群から選ばれた少なくとも1種である。

【0032】(b-1)フェノール系酸化防止剤：(b-1)フェノール系酸化防止剤は、フェノール基の2位および/または6位に、直鎖あるいは分岐を有する($\text{C}_{1}\sim\text{C}_{10}$)アルキル基が置換していることが特徴である。

(b-1)の具体例としては、ペンタエリスリチル-テトラキス〔3-(3,5-ジ-*t*-ブチル-4-ヒドロキシフェニル)プロピオネート〕、3,9-ビス〔2-(3-(3-*t*-ブチル-4-ヒドロキシ-5-メチルフェニル)プロピオニルオキシ)-1,1-ジメチルエチル〕2,4,8,10-テトラオキサスピロ〔5,5〕ウンデカン、オクタデシル-3-(3,5-ジ-*t*-ブチル-4-ヒドロキシフェニル)プロピオネート、1,6-ヘキサンジオール-ビス〔3-(3,5-ジ-*t*-ブチル-4-ヒドロキシフェニル)プロピオネート〕、1,3,5-トリメチル-2,4,6-トリス〔3,5-ジ-*t*-ブチル-4-ヒドロキシベンジル〕ベンゼン、2,6-ジ-*t*-ブチル-4-メチルフェノール、2,6-ジ-*t*-ブチル-4-エチルフェノール、2,6-ジフェニル-4-オクタデシロキシフェノール、ステアリル〔3,5-ジ-*t*-ブチル-4-ヒドロキシフェニル)プロピオネート、ジステアリル〔3,5-ジ-*t*-ブチル-4-ヒドロキシベンジル〕ホスホネート、チオジエチレングリコールビス〔(3,5-ジ-*t*-ブチル-4-ヒドロキシフェニル)プロピオネート〕、4,4'-チオビス〔6-*t*-ブチル-*m*-クレゾール〕、2-オクチルチオ-4,6-ジ〔3,5-ジ-*t*-ブチル-4-ヒドロキシフェノキシ〕-s-トリアジン、2,2'-メチレンビス〔4-メチル-6-*t*-ブチル-6-*t*-ブチルフェノール〕、2,2'-メチレンビス〔4-エチル-6-*t*-ブチルフェノール〕、ビス〔3,3-ビス〔4-ヒドロキシ-3-*t*-ブチルフェニル)ブチリクアシッド〕グリコールエステル、4,4'-ブチリデニビス〔6-*t*-ブチル-*m*-クレゾール〕、2,2'-エチリデニビス〔4,6-ジ-*t*-ブチルフェノール〕、2,2'-エチリデニビス〔4-s-ブチル-6-*t*-ブチルフェノール〕、1,1,3-トリス〔2-メチル-4-ヒドロキシ-5-*t*-ブチルフェニル)ブタン、ビス〔2-*t*-ブチル-4-メチル-6-(2-ヒドロキシ-3-*t*-ブチル-5-メチルベンジル)フェニル〕テレフタレート、1,3,5-トリス〔2,6-ジメチル-3-ヒドロキシ-4-*t*-ブチルベンジル)イソシアヌレート、1,3,5-トリス〔3,5-ジ-*t*-ブチル-4-ヒドロキシベンジル)-2,4,6-トリメチルベンゼン、1,3,5-トリス〔(3,5-ジ-*t*-ブチル-4-ヒドロキシフェニル)プロピオニルオキシエチル〕イソシアヌレート、テトラキス〔メチレン-3-(3,5-ジ-*t*-ブチル-4-ヒドロキシフェニル)プロピオネ

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ート)メタン、2-*t*-ブチル-4-メチル-6-(2-
-アクリロイルオキシ-3-*t*-ブチル-5-メチルベン
ンジル)フェノール、3,9-ビス(1,1-ジメチル
-2-ヒドロキシエチル)-2,4-8,10-テトラ
オキサスピロ[5,5]ウンデカン-ビス[β-(3-
-*t*-ブチル-4-ヒドロキシ-5-メチルフェニル)プロ
ピオネート]、トリエチレングリコールビス[β-
(3-*t*-ブチル-4-ヒドロキシ-5-メチルフェニル)
プロピオネート]、1,1'-ビス(4-ヒドロキシ
フェニル)シクロヘキサン、2,2'-メチレンビス
(4-メチル-6-*t*-ブチルフェノール)、2,2'-
10
'-メチレンビス(4-エチル-6-*t*-ブチルフェノ
ール)、2,2'-メチレンビス(6-(1-メチルシ
クロヘキシル)-4-メチルフェノール)、4,4'-
ブチリデンビス(3-メチル-6-*t*-ブチルフェノ
ール)、3,9-ビス(2-(3-*t*-ブチル-4-ヒド
ロキシ-5-メチルフェニルプロピオニロキシ)1,1-
-ジメチルエチル)-2,4,8,10-テトラオキサ
スピロ(5,5)ウンデカン、4,4'-チオビス(3-
-メチル-6-*t*-ブチルフェノール)、4,4'-
20
ビス(3,5-ジ-*t*-ブチル-4-ヒドロキシベンジ
ル)サルファイド、4,4'-チオビス(6-*t*-ブチ
ル-2-メチルフェノール)、2,5-ジ-*t*-ブチル
ヒドロキノン、2,5-ジ-*t*-アミルヒドロキノン、
2-*t*-ブチル-6-(3-*t*-ブチル-2-ヒドロキ
シ-5-メチルベンジル)-4-メチルフェニルアクリ
レート、2,4-ジメチル-6-(1-メチルシクロヘ
キシル、スチレネイテッドフェノール、2,4-ビス
(*o*-メチルチオ)メチル)-5-メチルフェノール、
などが挙げられる。これらの中では、ヒンダードフェ
ノール系酸化防止剤が好ましい。

【0033】(b-2)リン系酸化防止剤：(b-2)
リン系酸化防止剤は、III価のリン化合物であるホス
フェイト、あるいはホスフェートである。具体例として
は、ビス-(2,6-ジ-*t*-ブチル-4-メチルフェ
ニル)ペンタベンタエリスリトールジホスファイト、ト
リス(2,4-ジ-*t*-ブチルフェニルホスファイ
ト)、テトラキス(2,4-ジ-*t*-ブチル-5-メチ
ルフェニル)-4,4'-ビフェニレンジホスホナイ
ト、3,5-ジ-*t*-ブチル-4-ヒドロキシベンジル
ホスホネート-ジエチルエステル、ビス-(2,6-ジ
クミルフェニル)ペンタエリスリトールジホスファイ
ト、2,2'-メチレンビス(4,6-ジ-*t*-ブチルフェ
ニル)オクチルホスファイト、トリス(ミックスドモ
ノandジ-*n*-ニルフェニルホスファイト)、ビス
(2,4-ジ-*t*-ブチルフェニル)ペンタベンタエリ
スリトール-ジホスファイト、ビス(2,6-ジ-*t*-
ブチル-4-メトキシカルボニルエチルフェニル)
ペンタエリスリトールジホスファイト、ビス(2,6-
30
ジ-*t*-ブチル-4-オクタデシルオキシカルボニルエ

チルフェニル)ペンタエリスリトールジホスファイト
などが挙げられる。これらの中では、ホスファイトおよ
びホスフェートが好ましい。

【0034】(b-3)チオエーテル系酸化防止剤：
(b-3)チオエーテル系酸化防止剤の具体例として
は、ジラウリル3,3'-チオジプロピオネート、ビス
(2-メチル-4-(3-*n*-ドデシル)チオプロピオ
ニルオキシ)-5-*t*-ブチルフェニル)スルフィド、
ジステアリル-3,3'-チオジプロピオネート、ベン
タエリスリトール-テトラキス(3-ラウリル)チオプロ
ピオネートなどが挙げられる。

【0035】(B)酸化防止剤は、上記(b-1)フェ
ノール系酸化防止剤と(b-2)リン系酸化防止剤と
(b-3)チオエーテル系酸化防止剤を、それぞれ、単
独で、あるいは、併用して用いることができるが、好ま
しくは(b-1)成分と(b-2)または(b-3)成
分の2種以上の併用系が好ましい。これら酸化防止剤の
熱重量分析(TGA)における5%重量減の温度は250
℃以上が必要であり、さらに300℃以上が好ましい。
5%重量減の温度が250℃未満であるものは、ポリマ
ーを150℃以上の高温で使用した場合には揮発してしま
い、酸化防止剤の効果が無くなってしまふ。

【0036】また、本発明の耐熱性樹脂組成物における
(A)環状オレフィン系(共)重合体と(B)酸化防止
剤の使用割合は、(A)成分100重量部に対し、(B)
成分が、通常、0.05~5重量部、好ましくは0.3
~3重量部である。(B)成分の使用割合が、0.05
重量部未満では、充分な酸化劣化防止効果を得ることが
できず、一方5重量部を超えて添加すると、得られる組
成物の機械的強度やガラス転移温度などの品質の低下、
加熱時の揮発成分の増加などが生じてしまい、好ま
しくない。

【0037】(A)環状オレフィン系(共)重合体に、
これらの(B)酸化防止剤を添加する方法としては、特
定の環状オレフィン(1)や(2)の合成時または精製
時に添加する方法、環状オレフィン系(共)重合体溶液
に添加する方法、該(共)重合体の精製時に添加する方
法などが挙げられ、(共)重合体そのものに添加する以
外、溶媒などにあらかじめ添加しておくこともでき、特
に限定されるものではない。

【0038】なお、本発明の(A)環状オレフィン系
(共)重合体には、従来、公知の開環重合体の水素化物
であるノルボルネン系重合体や付加重合体〔例えば、特
開昭61-29260号公報、特開昭60-16870
号公報、特開昭60-26024号公報、特開平2-5
1511号公報、特開平1-132625号公報、特開
平1-132626号公報、特開平4-202404号
公報、特開平4-63807号公報、特開平8-198
919号公報、特表平9-508649号公報、特表平
11-505880号公報、特開昭61-292601

号公報など記載の(共)重合体]とブレンドして、得られる組成物に優れた耐熱性、光学特性(透明性、低複屈折性)、接着・密着性を付与することができる。

【0039】このような組成物において、本発明の(A)環状オレフィン系(共)重合体と他の重合体との配合割合は、本発明の(共)重合体および他の重合体の種類、両者の相溶性、組成物の使用目的に応じて、適宜選択されるが、優れた耐熱性を有する組成物を得るためには、本発明の(A)環状オレフィン系(共)重合体の割合が、好ましくは5~95重量%、さらに好ましくは10~90重量%、特に好ましくは20~80重量%である。

【0040】また、本発明の耐熱性樹脂組成物には、このほか光による樹脂の劣化を防止する効果のある安定剤を、耐熱性を損なわない範囲で1種または2種以上組み合わせて用いてもよい。安定剤として用いられるもののうち、紫外線吸収剤としては、ベンゾフェノン系、サルチレート系、ベンゾトリアゾール系などが挙げられる。以下に、安定剤の具体例を列記する。

【0041】アミン系安定剤としては、フェニル- α -ナフチルアミン、フェニル- β -ナフチルアミン、ジオクチルフェニルアミン、N, N'-ジフェニル-p-フェニレンジアミン、N', N'-ジ- β -ナフチル-p-フェニレンジアミン、N-シクロヘキシル-N'-フェニル-p-フェニレンジアミン、2-(3, 5- t -ブチル-4-ヒドロキシベンジル)-2-n-ブチルマロン酸ビス(1, 2, 2, 6, 6-ペンタメチル-4-ビペリジル)、ポリ{[6-(1, 1, 3, 3-テトラメチルブチル)イミノ-1, 3, 5-トリアジン-2, 4-ジイル][(2, 2, 6, 6-テトラメチル-4-ビペリジル)イミノ]ヘキサメチレン[(2, 2, 6, 6-テトラメチル-4-ビペリジル)イミノ]}、コハク酸ジメチル-1-(2-ヒドロキシエチル)-4-ヒドロキシ-2, 2, 6, 6-テトラメチルビペリジン重縮合物、ビス(2, 2, 6, 6-テトラメチル-4-ビペリジル)セバケートなどが挙げられる。

【0042】ベンゾフェノン系安定剤としては、2-ヒドロキシベンゾフェノン、2-ヒドロキシ-4-メトキシベンゾフェノン、2, 4-ジヒドロキシベンゾフェノン、2, 2', 4-トリヒドロキシベンゾフェノン、2, 2', 4, 4'-テトラヒドロキシベンゾフェノンなど挙げられる。

【0043】サルチレート系安定剤としては、フェニルサルチレート、2, 4-ジ- t -ブチルフェニル-3', 5'-ジ- t -ブチル-4'-ヒドロキシベンゾエート、フェニル-3, 5-ジ- t -ブチル-4-ヒドロキシベンゾエート、2-メチル-4- t -ブチルフェニル-3', 5'-ジ- t -ブチル-4'-ヒドロキシベンゾエートなどが挙げられる。

【0044】ベンゾトリアゾール系安定剤としては、2

-(2'-ヒドロキシ-5'-メチルフェニル)ベンゾトリアゾール、2-(2'-ヒドロキシ-3'- t -ブチル-5'-メチルフェニル)-5-クロロベンゾトリアゾール、2-(2'-ヒドロキシ-3'- t -ブチルフェニル)ベンゾトリアゾール、2-(2'-ヒドロキシ-5'- t -オクチルフェニル)ベンゾトリアゾール、2-(2'-3', 5'-ジ- t -アミルフェニル)ベンゾトリアゾールなどが挙げられる。

【0045】ヒドラジン系安定剤としては、マレイン酸ヒドラジド、N, N'-ビス[3-(3, 5-ジ- t -ブチル-4-ヒドロキシフェニル)プロピオニル]ヒドラジン、N-サリシロイル-N'-アルデヒドヒドラジンなどが挙げられる。

【0046】エポキシ系安定剤としては、エポキシ化アマニ油、エポキシ化大豆油、エポキシブチルステアレート、エポキシオクチルステアレート、エポキシラウリルステアレート、低分子量エポキシ樹脂などが挙げられる。以上の各安定剤は、1種または2種以上混合して用いられる。

【0047】本発明の耐熱性樹脂組成物には、さらに必要に応じて高級ジカルボン酸金属塩、高級カルボン酸エステルなどの滑剤、可塑剤、帯電防止剤、無機および有機系着色剤、発泡剤、無機および有機系充填剤、上記以外の難燃剤、表面光沢改良剤、艶消し剤などを添加することができる。これらの各種添加剤は樹脂組成物の製造工程中において添加することができる。

【0048】本発明の耐熱性樹脂組成物は、キャストリング時に、溶媒中に(A)環状オレフィン系(共)重合体および上記(B)酸化防止剤、さらに必要に応じて使用される添加剤を混合することによって得られる。キャストリング溶媒としては、(A)と(B)の両方が溶解するものが好ましい。

【0049】なお、本発明の耐熱性樹脂組成物は、単独で使用することができるが、各種極性材料との親和性が良好であることから、ガラス繊維、金属繊維、炭素繊維あるいはこれらの粉末、炭酸カルシウム、タルク、セッコウ、アルミナ、シリカ、雲母、チタ化ホウ素、ジルコニア、炭化ケイ素、チタン酸カリウムなどの複合材料として使用することもできる。

【0050】本発明の環状オレフィン系共重合体と酸化防止剤の耐熱性樹脂組成物は、高耐熱性の要求される用途、例えば液晶基板ガラスのプラスチック代替材料などに好適である。すなわち、液晶表示基板上へのTFT(薄膜トランジスタ)形成での露光、現像、エッチングなどの工程で基板材料に要求される耐熱性を満足させることができる。また、本発明の耐熱性樹脂組成物は、優れた光学透明性、耐熱性、接着・密着性、耐吸湿性を有するので、導光板、偏光フィルム、液晶パネル、位相差フィルム、透明導電性フィルム、OHPフィルム、光ディスク、光ファイバー、レンズなどの電子部品、医療

容器、容器などにも用いられる。

【0051】

【実施例】以下、実施例を挙げて本発明をさらに具体的に説明するが、本発明は以下の実施例に限定されるものではない。なお、実施例中、部および%は、特に断らないかぎり重量基準である。また、実施例中の重量平均分子量・数平均分子量、固有粘度、色相は、次のようにして測定したものである。

重量平均分子量・数平均分子量

ウォーターズ（WATERS）社製、150C型ゲルパーミエーションクロマトグラフィー装置で、東ソー（株）製のHタイプカラムを用い、o-ジクロロベンゼンを溶媒として、120℃で測定した。得られた分子量は、標準ポリスチレン換算値である。

色相

各種酸化防止剤をキャスト時にポリマー溶液に添加し、その均一溶液を用いてキャスト法にてフィルムを作成した。得られたサンプルをそれぞれ15%塩化メチレン溶液とし、JIS K7103に従って黄色度（YI値）を透過光で測定した。

【0052】合成例1

単量体として5-n-ヘキシル-2-ノルボルネン93.75ミリモル、2-ノルボルネン500ミリモル、5-トリエトキシシリル-2-ノルボルネン31.25ミリモル、溶媒として、トルエン500gを容量1リットルの反応器に窒素下で仕込んだ。反応系を10℃に調節し、トリエチルアルミニウム0.5ミリモル、三フッ化ホウ素・ジエチルエーテル（BF₃・Et₂O）0.4ミリモル、の順に添加し、最後に予めオクタン酸ニッケルと六フッ化アンチモン酸（HSbF₆）を-15℃でモル比1:1で反応させたニッケル化合物をニッケル原子で0.2ミリモル添加して重合を開始した。30℃で2時間重合を行い、エタノールで重合を停止した。共重合体への転化率は89%であった。この共重合体溶液に乳酸60ミリモルを加え、触媒成分と反応させた。共重合体溶液を5リットルのイソプロパノールに入れ、共重合体を凝固し、未反応の単量体、上記の反応試薬および触媒残さを共重合体から除去した。凝固した共重合体を乾燥し、共重合体Aを得た。A中のトリエトキシシリル基を含む構造単位の含有量は270MHz、¹H-NMR分析（4ppmのエトキシシリル基メチレン吸収、溶媒：D化トルエン、TMS基準）から4.9モル%であった。5-n-ヘキシル-2-ノルボルネンに由来する構造単位の含有量は赤外分析721cm⁻¹の特性吸収による検量線から、14.0モル%であった。GPCの測定から、共重合体Aのポリスチレン換算の数平均分子量は200,000、重量平均分子量は440,000であった。

【0053】合成例2

合成例1にて、5-n-ヘキシル-2-ノルボルネン1

25ミリモル、2-ノルボルネン500ミリモルを用いる以外、合成例1と同様に行い共重合体Bを得た。共重合体への転化率は92%であった。5-n-ヘキシル-2-ノルボルネンに由来する構造単位の含有量は赤外分析721cm⁻¹の特性吸収による検量線から、19.0モル%であった。共重合体Bのポリスチレン換算の数平均分子量は117,000、重量平均分子量は270,000であった。

【0054】合成例3

単量体として5-n-ヘキシル-2-ノルボルネン93.75ミリモル、2-ノルボルネン500ミリモル、8-メチル、8-メトキシカルボニル-3-テトラシクロ〔4.4.0.1^{2,3}.1^{7,8}〕ドデセン31.25ミリモルを用いる以外、合成例1と同様に行い共重合体Cを得た。共重合体への転化率は75%であった。C中の8-メチル、8-メトキシカルボニル-3-テトラシクロ〔4.4.0.1^{2,3}.1^{7,8}〕ドデセンに由来する構造体の割合は赤外分析1730cm⁻¹の特性吸収による検量線から、4.9モル%であった。5-n-ヘキシル-2-ノルボルネンに由来する構造体の含有量は、赤外分析の721cm⁻¹の特性吸収による検量線から14.5モル%であった。また、Cのポリスチレン換算の数平均分子量は、158,000、重量平均分子量は300,000であった。

【0055】合成例4

単量体として5-n-ヘキシル-2-ノルボルネン93.75ミリモル、2-ノルボルネン500ミリモル、5-エチリデン-2-ノルボルネン31.25ミリモルを用いる以外、合成例1と同様に行い共重合体Dを得た。共重合体Dへの転化率は80%であった。D中の5-エチリデン-2-ノルボルネンに由来する構造体単位の割合は、ヨウ素化滴定法により4.9モル%であった。5-n-ヘキシル-2-ノルボルネンに由来する構造体の含有量は、赤外分析の721cm⁻¹の特性吸収による検量線から14.0モル%であった。共重合体Dの数平均分子量は138,000、重量平均分子量は290,000であった。

【0056】キャスト法による製膜例

上記各合成例で得られた環状オレフィン系共重合体をトルエンに溶解させ、TSC=10%となる様に調製した。この溶液を1マイクロメートルメッシュのフィルターでろ過した後、種酸化防止剤（b-1）、（b-2）、および（b-3）を下表1で示す量添加し、均一溶液とした。これをステンレス基板上に塗布した後、室温下で溶媒を気化させた。得られたフィルムを、真空中、210℃で2時間加熱処理する事でフィルム中に残存している溶媒を完全に気化させ、目的の透明フィルムが得られた。

【0057】実施例1~23、比較例1~3

上記キャスト法により得られた透明フィルムを空気中で加熱し、耐酸化劣化性を色相(YI値)の変化により評価し

た。また、表2～5 中で使用された(b-1), (b-2), (b-3) の各種酸化防止剤の詳細は、次の通りである。

(b-1) 成分; フェノール系酸化防止剤

a: ペンタエリスリチル-テトラキス[3-(3,5-ジ-*tert*-ブチル-4-ヒドロキシフェニル)プロピオネート

b: 1,3,5-トリメチル-2,4,6-トリス(3,5-ジ-*tert*-ブチル-4-ヒドロキシベンジル)ベンゼン

c: オクタデシル-3-(3,5-ジ-*tert*-ブチル-4-ヒドロキシフェニル)プロピオネート

d: 2,6-ジ-*tert*-ブチル-4-メチルフェノール

(b-2) 成分; リン系酸化防止剤

* e: ビス(2,6-ジ-*tert*-ブチル-4-メチルフェニル)ペンタエリスリトール-ジ-ホスファイト

f: テトラキス(2,4-ジ-*tert*-ブチル-5-メチルフェニル)-4,4'-ビフェニレンジホスホナイト

g: トリス(2,4-ジ-*tert*-ブチルフェニル)ホスファイト

h: 2,2-メチレンビス(4,6-ジ-*tert*-ブチルフェニル)オクチルホスファイト

(b-3) 成分; チオエーテル系酸化防止剤

i: ビス(2-メチル-4-(3-*n*-ドデシル)チオプロピオニルオキシ)-5-*tert*-ブチルフェニル)スルフィド

[0058]

* [表1]

熱重量分析(TGA)での各酸化防止剤(B)の5%重量減少温度(℃)

| 酸化防止剤(B) | | 5% loss温度(℃) |
|----------|---|--------------|
| b-1 | a | 322 |
| | b | 342 |
| | c | 274 |
| | d | 85 |
| b-2 | e | 301 |
| | f | 305 |
| | g | 289 |
| | h | 285 |
| b-3 | i | 265 |

[0059]

※ ※ [表2]

酸化防止剤 b-1 ~ b-3をそれぞれ単独でベースポリマー(A) ($M_w=44 \times 10^4$)に添加した時の、air下での酸化防止効果

| 実施例 | 酸化防止剤 | | 200℃×1 hr 加熱後 | | 240℃×1 hr 加熱後 | |
|-------|---------|------------|----------------|-------------------|----------------|-------------------|
| | 種類 | 量 (phr) | 色相の変化 (YI値) | $M_w \times 10^4$ | 色相の変化 (YI値) | $M_w \times 10^4$ |
| 1 | a (b-1) | 0.9 | 0 | 44 | 17 | 12 |
| 2 | b (b-1) | 0.9 | 0 | 44 | 17 | 12 |
| 3 | c (b-1) | 0.9 | 0 | 42 | 18 | 10 |
| 4 | d (b-1) | 0.9 | 0 | 40 | 18 | 10 |
| 5 | e (b-2) | 0.9 | 0 | 44 | 18 | 10 |
| 6 | f (b-2) | 0.9 | 0 | 44 | 18 | 10 |
| 7 | g (b-2) | 0.9 | 0 | 44 | 18 | 10 |
| 8 | h (b-2) | 0.9 | 0 | 44 | 18 | 10 |
| 9 | i (b-3) | 0.9 | 0 | 44 | 18 | 10 |
| 比較例-1 | ブランク | 0 | 15 | 16 | 18 | 10 |

[0060]

[表3]

酸化防止剤 b-1 ~ b-3を組み合わせてベースポリマー(A) ($M_w=44 \times 10^4$) に
添加した時の、air下での酸化防止効果

| 実施例 | 酸化防止剤 | | 200℃×1 hr 加熱後 | | 240℃×1 hr 加熱後 | |
|-----|-------------------|---------|---------------|-------------------|---------------|-------------------|
| | 種類 | 量 (phr) | 色相 (YI値) | $M_w \times 10^4$ | 色相 (YI値) | $M_w \times 10^4$ |
| 10 | a (b-1) + e (b-2) | 各々0.9 | 0 | 44 | 0 | 43 |
| 11 | b (b-1) + f (b-2) | 各々0.9 | 0 | 44 | 0 | 43 |
| 12 | c (b-1) + g (b-2) | 各々0.9 | 0 | 44 | 6 | 33 |
| 13 | d (b-1) + h (b-2) | 各々0.9 | 0 | 44 | 7 | 31 |
| 14 | a (b-1) + i (b-3) | 各々0.9 | 0 | 44 | 8 | 29 |

【0061】

* * 【表4】

酸化防止剤 (a (b-1)+ e (b-2))の添加量の違いによる酸化防止効果
(ベースポリマー(A) ($M_w=44 \times 10^4$))

| 実施例 | 酸化防止剤 | | 200℃×1 hr 加熱後 | | 240℃×1 hr 加熱後 | |
|-------|---------------------|---------------------|---------------|-------------------|---------------|-------------------|
| | a (b-1) の量 (phr) | e (b-2) の量 (phr) | 色相 (YI値) | $M_w \times 10^4$ | 色相 (YI値) | $M_w \times 10^4$ |
| 15 | 0.1 | 0.1 | 0 | 43 | 17 | 12 |
| 16 | 0.1 | 0.3 | 0 | 43 | 11 | 23 |
| 17 | 0.3 | 0.9 | 0 | 43 | 2 | 40 |
| 18 | 0.9 | 0.9 | 0 | 44 | 0 | 43 |
| 19 | 0.9 | 0.1 | 0 | 43 | 14 | 18 |
| 比較例-2 | 0.02 | 0.02 | 14 | 17 | 17 | 12 |
| 比較例-3 | 5.0 | 5.0 | 0 | 44 | 0 | 44 |

※ 比較例3では、240℃×1 hr 加熱後にサンプル重量が2%減少

【0062】

* * 【表5】

ベースポリマー(A~E) に対する 酸化防止剤 [a (b-1)+ e (b-2)] の効果

(a: 0.9 phr, e: 0.9 phr)

| 実施例 | ポリマー | 加熱前の $M_w \times 10^4$ | 200℃×1 hr 加熱後 | | 240℃×1 hr 加熱後 | |
|-----|------|---------------------------|---------------|-------------------|---------------|-------------------|
| | | | 色相 (YI値) | $M_w \times 10^4$ | 色相 (YI値) | $M_w \times 10^4$ |
| 20 | A | 44 | 0 | 44 | 0 | 43 |
| 21 | B | 27 | 0 | 27 | 0 | 26 |
| 22 | C | 30 | 0 | 30 | 0 | 29 |
| 23 | D | 29 | 0 | 29 | 0 | 27 |

【0063】

【発明の効果】本発明の耐熱性樹脂組成物は、充分に高いガラス転移温度を有する環状オレフィン系(共)重合体に特定の酸化防止剤を組み合わせることにより、酸化劣化によって起こる着色が大幅に改良され、従来問題とな

っている過酷な条件下での黄変色の問題を解決するものである。本技術の開発により、これまでの樹脂では耐熱性の点で不可能であった、TF T液晶のガラス基板のプラスチック化、高い耐熱性と透明性を有する半導体封止剤、などが可能となる。

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